Carnegie Institution of Washington
Washington, DC

Astrobiological Pathways: From the Interstellar Medium, through Planetary Systems, to the Emergence and Detection of Life

Principal Investigator:

Sean Solomon scs@dtm.ciw.edu

Co-Investigators/Collaborators:

At Carnegie Institution of Washington:
Conel Alexander
Alan Boss
R. Paul Butler
George Cody
Marilyn Fogel
Erik Hauri
Robert Hazen
Russell Hemley,
Wesley Huntress
Larry Nittler
Douglas Rumble
James Scott
Sara Seager
Andrew Steele
Alycia Weinberger
George Wetherill
Hatten Yoder

John Baross, *University of Washington*
Jay Brandes, *University of Texas, Austin*
David Deamer, *University of California, Santa Cruz*
David Emerson, *ATCC*
James Farquhar, *University of Maryland, College Park*
Timothy McCoy, *Smithsonian Institution*
Rhonda Stroud, *US Naval Research Laboratory*
Noreen Tuross, *Smithsonian Institution*
Ed Vicenzi, *Smithsonian Institution*

Table of Contents

Volume I Page

3. Executive Summary

Unifying Intellectual Focus. The NASA Astrobiology Institute team led by the Carnegie Institution will be dedicated, over the coming five years, to the study of the gradual evolution of organic compounds from prebiotic molecular synthesis and organization to cellular evolution and diversification – processes central to the missions of the NAI. Our program attempts to integrate the sweeping narrative of life's history through a combination of bottom-up and top-down studies. On the one hand, we study processes related to chemical and physical evolution in plausible prebiotic environments – the interstellar medium, circumstellar disks, extrasolar planetary systems, and the primitive Earth. Complementary to these bottom-up investigations of life's origin, we will continue our field and experimental top-down efforts to document the nature of microbial life at extreme conditions, as well as the characterization of organic matter in ancient fossils. Both types of efforts inform our development of biotechnological approaches to life detection on other worlds. In the process, we will continue to serve as a resource center for all members of the NASA Astrobiology Institute.

Motivation and Rationale. The most compelling opportunities in astrobiology stem from new interdisciplinary approaches to fundamental questions about life's origin and its distribution in the universe. We continue to be motivated by the importance of these questions and by our unusual interdisciplinary team approach to scientific research. The Carnegie Institution supports astrobiologists with backgrounds in astronomy, biology, geology, and chemistry on a single Washington, D.C., campus. We are motivated to make additional progress toward addressing these fundamental questions, while continuing to serve as a dynamic, interactive resource center for other NAI teams. The rationale for our proposal is guided by the visionary mission of NASA's Astrobiology Program, as defined by the Astrobiology Roadmap. In particular, we address the nature and distribution of planets (Goal 1), past and present habitable environments (Goal 2), the chemical origin of life (Goal 3), past life on Earth (Goal 4), the environmental limits on life (Goal 5), and the identification and detection of biosignatures (Goal 7). Moreover, through our daily interactions we will continue to strive to integrate these separate goals into a fuller understanding of the continuous processes that characterize life's origin, evolution, and distribution in the universe.

Proposed Research Plan. Our proposed research activities for the coming five years focus on life's chemical and physical evolution, from the interstellar medium, through planetary systems, to the emergence and detection of life. We propose seven integrated areas of research:

1. We will continue to apply theory and observations to investigate chemical evolution in the interstellar medium, in circumstellar disks, during planetary formation, and on Solar System bodies.

2. We will conduct analytical research on extraterrestrial samples, including meteorites and interplanetary dust particles, with an emphasis on organic molecules and evidence for water.

3. We will study prebiotic chemical and isotopic evolution on Earth, with a new emphasis on the sulfur cycle and the role of sulfur in prebiotic organic synthesis.

4. We will investigate possible mechanisms of prebiotic molecular selection and macromolecular organization, including the self-organization of amphiphiles and the selective adsorption of organic molecules onto mineral surfaces.

5. We will continue to study life in extreme environments, with field studies of hydrothermal microbial communities and laboratory studies of stress adaptation of microbes in high-pressure and high-temperature environments.

6. We will examine ancient fossils and microbes fossilized in the laboratory with a variety of analytical techniques to assess preservation mechanisms of molecular biosignatures. We will study modern geothermal systems to investigate preservation of biosignatures during silicification in these environments.

7. We will apply our enhanced understanding of life's chemical and physical evolution to develop new techniques in astrobiotechnology – procedures that will be applied to the design and testing of instruments for life detection, initially in terrestrial settings and eventually on spacecraft to be sent to other Solar System bodies.

Fuller understanding of life's origin, evolution, and distribution requires major advances on all these topics, as well as the extensive challenge of integrating these topics. During the next five years of NAI support we anticipate significant progress in each of these seven areas, as well as considerable advances derived from integrating these theoretical, experimental, and field studies.

Training, Education, and Public Outreach. As members of the NASA Astrobiology Institute we will continue our firm commitment to a dynamic, sustained program of education, public outreach, and training at the K-12, undergraduate, graduate, and postgraduate levels. This effort is facilitated by our widely acknowledged programs, including the First Light Science School, the Carnegie Academy for Science Education (CASE), the Carnegie Institution Summer Intern Program, and the Capital Science Lecture Series. Our continuing NAI outreach programs will include the following:

- We will continue to introduce astrobiology themes to CASE, which will provide in-service training and summer workshops for more than 1,000 teachers in the District of Columbia Public School system.

- We will introduce astrobiology themes to our widely distributed educational product series, as well as our astrobiology web site.

- The Carnegie Institution will continue to sponsor general audience lectures by prominent astrobiologists through the successful Capital Science public lecture series at Carnegie's headquarters in northwest Washington, D.C.

- We will initiate collaborative activities with the Minority Institution Astrobiology Collaborative, including research, internships, teacher training, and publications.

- We will develop an exhibition on astrobiology in the lobby of the Smithsonian Institution's National Museum of Natural History, one of the most frequently visited museums in the world.

- We will support approximately 8 NAI summer interns per year as part of the Carnegie Institution's program for undergraduate and high school students. This astrobiology program has already produced one Intel finalist and one Westinghouse finalist.

- We will support approximately 12-15 NAI Pre- and Postdoctoral Fellows per year.

- We will participate through teaching and research opportunities with the new Astrobiology Ph.D. program at George Mason University. The first Ph.D. candidate will be commencing research at Carnegie in the summer of 2003.

Management Plan. All investigators and collaborators have clearly defined roles and responsibilities. Team activities will be managed by an Executive Committee, consisting of representatives from the partner institutions and chaired by the Principal Investigator. Our plan for multi-institutional cooperation and coordination includes regular all-consortium symposia, frequent intersite lectures, regular visits of senior staff to partner institutions, and more extended exchanges of students, predoctoral scholars, and other staff. Through the use of the internet, the World Wide Web, and the next generation internet, we will continue to make extensive use of electronic communication. Beyond daily communications among individuals, we will continue to provide frequent Web-based news updates to all team members. We remain committed to the development of Web-based instructional and outreach materials, and we will continue our development of electronic communications to enable access to data archives and summaries of research activities.

Proposed Institutional Commitment. The Carnegie Institution will continue to make a substantial commitment of resources to astrobiology. Dr. Wesley Huntress, who initiated the Astrobiology Institute while at NASA's Office of Space Science, was selected as Director of the Geophysical Laboratory in 1998. Subsequently, the institution has added six astrobiologists to the senior scientific staff (Paul Butler, Larry Nittler, James Scott, Sara Seager, Andrew Steele, and Alycia Weinberger). The institution will provide full salary support for all 16 members of the senior research staff who are investigators on this project, 50% of the stipends of all NAI-sponsored Postdoctoral Research Associates, support for half of the 8 college and high-school astrobiology summer interns, and full support of all NAI-related technicians and Information Technology staff. An array of laboratory instrumentation with an aggregate value in excess of $10 million will continue to be made freely available to research in support of NASA Astrobiology Institute objectives. The Carnegie Institution will continue as well its major financial commitment to programs in science education and outreach. Significant contributions of salary support and laboratory instrumentation and facilities will also be made by each of the partner institutions in our consortium.

Innovation and Distinguishing Features. Our NAI team is distinguished by several features:

- Scientific breadth: We integrate experimental, theoretical, observational, and field studies by experts in astronomy, biology, geochemistry, organic chemistry, mineralogy, planetary science, microbial ecology, and biotechnology in one laboratory.

- Scientific focus: We direct this broad expertise toward fundamental astrobiological questions regarding the origin and distribution of life in the universe.

- Shared resources: We provide important resources for the larger astrobiology community. During the first five years of the NAI we hosted more than 30 researchers from other NAI teams, NAI foreign associates, and other institutions with interests in astrobiology.

- E/PO: Our consortium is dedicated to training, education, and outreach programs that reach numerous students, teachers, and members of the general public.

Summary. The mission of the Carnegie Institution's vibrant astrobiology program matches that of the NASA Astrobiology Institute itself – to explore the origins and distribution of life in the universe. Throughout the past five years the Carnegie team has played a significant and expanding role in shaping the context and content of NAI. Our dynamic and extensive research program, our acclaimed education and public outreach efforts, and our unswerving commitment to the future of astrobiology provide the primary motivations for this proposal. We look forward with enthusiasm to continued participation in this unique program.

5. Research and Management Plan

5.1 Introduction

Astrobiology, the search for the origin and distribution of life in the universe, demands a bold, interdisciplinary research strategy. Life's sweeping story began in the icy near-vacuum of the interstellar medium and the dynamic environments of circumstellar disks, where organic molecules first were formed and concentrated. Life emerged by the diverse chemical and physical processes of nascent planets and moons, and it continues to evolve in concert with its home world, on Earth, and perhaps elsewhere in the Cosmos. To explore such a history requires the integration of forefront research in astronomy, chemistry, planetary sciences, and biology. Here, we propose such a far-reaching effort.

Life's origin remains a mystery, but all life as we know it requires an environment with three key ingredients: energy, water, and access to the critical elements from which biochemistry is assembled. Our proposal outlines a narrative that traces the gradual evolution from prebiotic molecular synthesis and organization to cellular evolution and diversification.

We propose to begin our study of life's origin with investigations of the chemical evolution of the interstellar medium and circumstellar disks – environments in which simple organic molecules first appeared and concentrated. We also propose to consider the fate of this organic matter during planetary formation through observations of extrasolar planets and models of planetary system formation. These studies will be informed by our ongoing analytical research on organic molecules and evidence for water in extraterrestrial samples, including meteorites and interplanetary dust particles.

Life's narrative continues via prebiotic molecular evolution on Earth, a subject that has inspired a half-century of chemical research. We propose to expand our investigations into the role that transition-metal minerals may have played in promoting key prebiotic organic reactions. Such chemistry is closely connected to the chemical and isotopic evolution of Earth's sulfur cycle, which provides a key to understanding global geochemical and biochemical changes during Earth's first 3 billion years. Additionally, we will evaluate processes by which specific prebiotic organic species (such as chiral molecules) were selected, concentrated, and organized into macromolecular systems, both through molecular self-organization and selective adsorption on mineral surfaces.

Complementary to these bottom-up investigations of life's origin, we will continue our top-down efforts to document the nature of microbial life at extreme temperatures and pressures, including field studies of hydrothermal environments at deep-sea hydrothermal vents and in the newly opened hydrothermal district of Kamchatka. Fieldwork will be complemented by laboratory studies of high-pressure microbial survival and adaptation. We will also focus on pathways of microbial metabolism – processes that influence the evolution of planetary environments.

Our proposed studies of prebiotic organic chemistry and microbial biochemistry inform the search for life on other worlds. We therefore propose to continue attempts to identify reliable biosignatures by measuring elemental, isotopic, and molecular characteristics of ancient fossils and to compare these results with measurements of abiotic suites of organic species derived from carbonaceous meteorites and our organic synthesis experiments. These studies will guide our development of analytical techniques for remote detection of biosignatures on space flight missions.

This ambitious program of research is enabled, in part, by the unusual degree of scientific integration of the Carnegie Institution team. Since 1998 the Carnegie Institution has added six new staff scientists in key astrobiology fields, including planet formation, detection of extrasolar planets, cosmochemistry, microbial ecology, extremophiles, and life detection. We enjoy an unusual degree of interdisciplinary interaction and collaboration because these scientists have offices and laboratories on Carnegie's close-knit Broad Branch Road campus in Washington, D.C. In addition to the core team of 18 Carnegie astronomers, chemists, planetary scientists, and biologists, we have invited nine scientists from seven partner institutions to fill key gaps in the narrative of life's origin and evolution.

Funding of this proposal will result in at least three important benefits to the NASA Astrobiology Institute. First, this proposal describes an integrated program of research that will not be attempted without NAI support. Most Carnegie NAI Investigators are engaged in several other research activities as well as astrobiology. We estimate that as many as half of the nearly 200 NAI-sponsored peer-reviewed articles (**Section 14**) produced by Carnegie team members between 1998 and 2003 (including all of the work by NAI-supported undergraduate, predoctoral, and postdoctoral fellows) would not have been completed without NAI funding.

Second, NAI fosters our interdisciplinary team approach to astrobiology research. The daily on-campus interactions among astronomers, chemists, planetary scientists, and biologists are an important outcome of NAI's sponsorship, and they have influenced strongly each individual's approach to the field. Thanks to NAI support, many collaborative cross-disciplinary projects have resulted. The net scientific contribution is greater than the sum of the parts.

Thirdly, thanks to NAI, Carnegie scientists have increasingly taken leadership roles in the astrobiology community. In addition to Carnegie's exemplary Education and Public Outreach efforts, team scientists have delivered more than 100 public lectures on astrobiology topics and have participated widely in meetings on astrobiology themes. For example, the Carnegie Institution hosted the April 2001 General Meeting of NAI in Washington, D.C., where they contributed 20 oral and poster presentations. At the February 2003 NAI General Meeting in Tempe, Arizona, Carnegie scientists and their team colleagues participated in 33 oral and poster presentations – more than 15% of the presentations at that meeting.

Astrobiologists pose profound questions about life's origin and cosmic distribution. Significant progress toward the field's inspiring goals will require broad vision, effective interdisciplinary collaboration, and the hard work of many dedicated scientists. With NAI support we will continue to strive toward those goals.

The format of the research section of this proposal breaks the discussion into seven scientific focus areas, each self-contained with the essential background material and specific proposed research. Because there is considerable synergy across the various scientific focus areas, we highlight where research in each section connects with other proposed research. Our Management Plan (**Section 5.9**) describes in detail how we will integrate these scientific initiatives into an effective element of NAI.

5.2 From Molecular Clouds to Habitable Planetary Systems

How far does prebiotic carbon chemistry advance in developing complex organic compounds in astronomical environments? Terrestrial life is carbon-based, and extraterrestrial life may be as well. Organic compounds are composed predominantly of carbon and hydrogen, but also oxygen, nitrogen, and sulfur. These five elements (CHONS) provide the most basic chemical prerequisites for life. Forged as elements in stellar interiors, carbon, oxygen, nitrogen, and sulfur undergo considerable chemical evolution in both diffuse and dense interstellar clouds (e.g., Prasad & Huntress 1980). Over 100 different molecules, produced by a variety of gas-phase and gas-grain interactions (e.g., Langer et al. 2000), have been detected in interstellar and circumstellar gas and dust clouds. Deciphering how the CHONS elements evolved from their astronomical origins to their participation in living organisms on habitable planets constitutes one of the most fundamental questions of astrobiology.

5.2.1 Protoplanetary and debris disks (Astrobiology Roadmap Objective 3.1)

Background. The link between the material of the interstellar medium and the ultimate composition of planets lies in the manner material is processed in circumstellar disks. The very different bulk compositions of the terrestrial, gas giant, and ice giant planets, as well as the asteroids and Kuiper Belt objects, must arise from some combination of segregation and survival of material in the early solar nebula and planet formation processes. We need to understand the evolution of the chemical content of planet-forming disks as a function of both location and time.

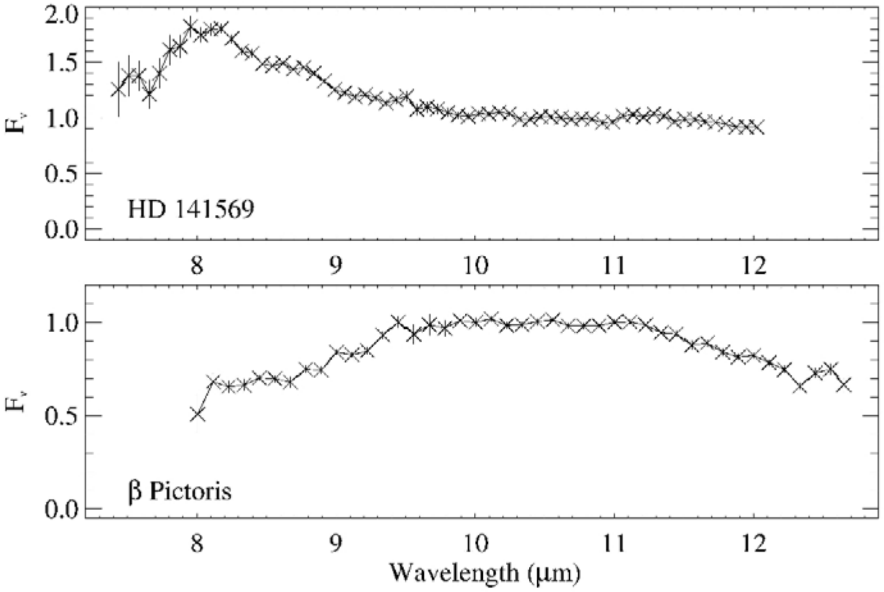

Figure 5.2.1. Spectra taken in the mid-infrared from the W. M. Keck Observatory, normalized arbitrarily at 11 μm. Top panel shows the 8-13 μm spectrum of HD 141569A, a 5-Myr old star approximately 20 times as luminous as the Sun. A prominent peak at 7.8 μm as well as a shoulder at 8.6 μm are evidence for PAH emission. However, the usually strong 11.2 μm PAH peak is not present. The line ratios suggest that the PAHs in this disk are both large and highly ionized. The bottom panel shows a spectrum of Beta Pictoris, a 12-Myr old star approximately 7 times as luminous as the Sun. Here silicate grains produce the broad peak centered at ~10 μm and there is no evidence for PAHs (Weinberger et al. 2003).

The infrared (IR) is an excellent wavelength range for studying the compositions of intermediate-age circumstellar disks (those in the process of losing their gas). Grains at temperatures of several hundred Kelvin, typical for dust at distances of 1-50 AU from the central star, emit strongly in the IR. Thus, IR emission emanates from dust grains in the region where planets formed in our own planetary system. Circumstellar disks are also known to be composed of materials, such as silicate grains, water and methane ices, and polycyclic aromatic hydrocarbons (PAHs), which have spectral features in the 1.5-25 μm (near-IR to mid-IR) region. Water ice is the most commonly detected material on surfaces in the outer Solar System and is found everywhere from comets, to the surfaces of satellites, to the small particles in the rings of the giant planets (Clark 1980; Irvine et al. 2000; Brown et al. 2000). Methane ice is less prevalent but is still the dominant feature in the spectrum of Pluto (Cruikshank et al. 1976). Methane may be quite common on the surfaces of Kuiper Belt objects. In disks, whether methane or water ice is more abundant may depend on progenitor cloud chemistry, the size of the bodies (Pluto's surface is covered mostly with methane ice and smaller Charon's with water ice), or distance from the central star. Ices were proposed to explain the high visual and near-infrared albedos of large (>1 µm) disk grains, which are typical for the ice-silicate mixtures in our own Solar System, and to explain an increase in the surface brightness of the disk around HD 141569A at the ice-condensation radius (Weinberger et al. 1999). Determining the location of ices in circumstellar disks requires high-dynamic-range spectrometry in the near-IR.

Perhaps the most striking feature of spectra from circumstellar disks that emit strongly in the mid-IR (8-24 µm) is how varied they are. About two-thirds show evidence of PAHs (Figure 5.2.1), independent of the host star’s spectral type, a few show very strong silicate features, and some show almost no silicate features. It is unclear why PAHs should dominate the spectra of some disks, while silicates should be most prevalent in others. The presence of PAHs probably indicates active chemistry occurring in the very inner parts of the disk. It may be that silicate grains are present in all intermediate-age disks but are large and cold, and therefore less efficient emitters in the mid-IR.

Research to Date. Detailed chemical studies of protoplanetary disks are hampered by the distance to even the nearest stellar nurseries, the T Tauri associations (~150 pc). At these distances, the 1-AU length scales that are necessary for studying inner disk processes are effectively unresolvable, even with the largest existing telescopes. Co-I Weinberger has published spatially resolved, mid-infrared spectra on the one disk for which the largest telescopes in the world have adequate spatial resolution (Weinberger et al. 2003); see Figure 5.2.1. She has been working on disk detection and spatially unresolved spectra in other nearby young stars (e.g., Weinberger et al. 2002). She has further proposed to use the Hubble Space Telescope (HST) for near-infrared imaging as a first attempt to detect water and methane ices in circumstellar disks.

Proposed Research. Co-I Weinberger will integrate her high-resolution mid-IR studies of disks into Carnegie’s multidisciplinary effort directed at constraining the origins and evolution of chondritic organic carbon (see **Sections 5.3.1 and 5.3.2**). Specifically, Weinberger will seek to determine the spatial distribution of PAH emission (a proxy for presolar organic carbon) within circumstellar disks. She will also constrain the size and ionization distribution of PAH molecules using the ratios of 7.7, 11.2, and 12.7 µm PAH features (Allamandola et al. 1999). If the fraction of ionized PAHs can be calculated, based on the observed stellar ultraviolet (UV) flux, then it will be possible to determine the radial distribution of PAHs in the disk, even though discrete PAH spectra remain spatially unresolved. Weinberger will develop new techniques for spatially resolved, near-IR spectroscopy of nearby circumstellar disks. She has applied for HST observation time for preliminary work on this project. Her ultimate goal is to develop an IR spectrograph for Carnegie's Magellan telescopes to work behind an adaptive optics (AO) system. This should allow for observations with a resolution of a few AU in the nearest young disks. Weinberger will work on techniques for obtaining the high-contrast spectra with Magellan AO that are necessary for studying faint disks around bright stars. The funds for building the new IR spectrograph will come from other sources. An NAI Postdoctoral Fellow with instrumental expertise would be an integral part of this development effort.

5.2.2 Formation of habitable planetary systems (Astrobiology Roadmap Objective 1.1)

Background. The conventional view of Solar System formation is that the presolar cloud collapsed in a region of low-mass star formation, similar to Taurus-Auriga (Shu et al. 1993). In such a quiescent setting, the background UV flux is likely to be low and limited largely to the flux from the proto-Sun, once it forms, greatly restricting the UV flux available for prebiotic chemistry.

Research to Date. A new scenario for Solar System formation has been proposed by Co-Is Boss and Wetherill and NAI Postdoctoral Fellow Haghighipour (Boss et al. 2002), based on forming the Solar System in a region of high-mass star formation, similar to the Orion Nebula cluster, and on the rapid formation of giant gaseous protoplanets by the disk instability mechanism (e.g., Boss 1997). This scenario relies upon a high flux of UV radiation from nearby massive stars to remove the gaseous portion of the solar nebula from Saturn's orbit and beyond and then to strip the gaseous envelopes from the outermost giant gaseous protoplanets, leaving behind largely ice and rock cores similar to what may have evolved into the ice giant planets, Uranus and Neptune. Terrestrial planet formation is likely to proceed largely unimpeded and may even be somewhat hastened by the gravitational perturbations from a rapidly formed Jupiter (Kortenkamp et al. 2001). Because the inner Solar System is deep within the Sun's gravitational potential well, a halo of hydrogen gas will be retained inside 10 AU, which will protect the planetesimals and gases of the inner solar nebula. Planetesimals and cometesimals outside this distance will be subjected to a withering UV flux once the disk gas in their vicinity has been photoevaporated.

If this new scenario can be shown to be applicable to the origin of the Solar System, then the implications for the frequency of habitable planets are clearly significant. Most stars are believed to form in regions of high-mass star formation, with perhaps only a minor fraction forming in regions similar to Taurus-Auriga. If the Solar System formed in a region similar to Orion, then the prospects for finding and characterizing other Earth-like planets increase several-fold. Future astrobiology space missions such as Kepler will determine the frequency of Earth-like planets and help to determine if this optimistic conjecture is correct.

Proposed Research. Co-I Boss receives support from NASA's Planetary Geology and Geophysics program to investigate the implications of this new scenario for planetary system formation. Boss and an NAI Postdoctoral Fellow will explore the implications of this new scenario for Solar System formation as a part of the Carnegie NAI effort. UV photons from nearby massive stars result in photolysis of the ices on the surfaces of cometesimals, producing PAHs and amino acids (Bernstein et al. 2002), i.e., a thick layer of organic compounds that will form an effective sun block. Beneath this surface layer, the pristine nature of these bodies will be retained. This scenario suggests that prebiotic UV-driven chemistry would have been vigorous in the outer regions of the solar nebula, even as the planetary accumulation process was underway. Because UV radiation can destroy as well as create organics, the outer solar nebula offers a perhaps unique opportunity to create complex organic compounds and to shelter them from subsequent UV-driven losses, though storage in cometesimals. Boss and an NAI Postdoctoral Fellow will model these processes in the context of Boss’s three dimensional, radiative, gravitational hydrodynamics models of the solar nebula.

Co-I Wetherill will continue to collaborate with Satoshi Inaba and Masahiro Ikoma of the Tokyo Institute of Technology in developing theoretical models for the formation of the gas giant planets Jupiter and Saturn by the alternative core accretion mechanism (Inaba et al. 2003b). This work has evolved to include calculating the importance of the early phase of formation of the atmosphere of these planets (Inaba et al. 2003a). Although volumetrically small in comparison to the eventual massive gaseous atmospheres of the gas giant planets, the early atmosphere has a profound influence on the growth rate of the solid cores and, furthermore, enhances the probability of collisions between the planetary embryos. These early atmospheres may exert a significant influence on the growth rate of the subsequent final giant planets and thus set the stage for the emergence of habitable terrestrial planets (Wetherill 1996).

5.2.3 Searching for extrasolar habitable planetary systems (Astrobiology Roadmap Objective 1.2)

Background. The ultimate goal of NASA's Navigator Program is to detect and characterize habitable terrestrial planets (Beichman et al. 1999). Achieving this extraordinarily ambitious goal requires the detection of nearby stars that are capable of sheltering Earth-like planets, i.e., stars with long-period Jupiter-mass planets – Jupiter intercepts Oort Cloud comets that would otherwise catastrophically impact the Earth (Wetherill 1994a).

Research to Date. Co-I Butler's Extrasolar Planet Search is designed to survey the nearest 1,300 Sun-like stars (F8-M5) with the precision Doppler technique at the Lick 3-m, Keck 10-m, and Anglo-Australian 3.9-m telescopes. Over the past 7 years, these surveys have led to the discovery of two-thirds of the known extrasolar planets, including the only known transit planet, all 5 published multiple planet systems, and all 5 published sub-Saturn-mass planets (e.g., Butler et al. 2003).

Most of the known planets orbit beyond 0.2 AU in eccentric ($e > 0.1$) orbits, while a surprising class of Jupiter-mass planets is found in circular orbits with periods of 3 to 5 days. Within the last year a handful of planets have been found orbiting beyond 1 AU in relatively circular orbits, suggesting that circular orbits may be more common among systems in which giant planets orbit in distant Jupiter-like orbits. Unfortunately, none of these planetary systems are hospitable to habitable Earths, because their present giant planet orbits would prevent an Earth from orbiting stably in the habitable zone (i.e., where liquid water can exist on the planet), because their orbits would have prevented an Earth from forming in the first place (Wetherill 1996), or because their inward migration to their present short-period orbits would have disrupted the formation of Earths in the habitable zone. However, less than 10% of nearby stars seem to be inhospitable to Earths – the remaining 90% could shelter exact Solar System analogues and we would not yet know it.

Proposed Research. The long-term goal of Co-I Butler's work is to survey all 2,000 nearby Sun-like stars out to 50 parsecs. Butler will begin adding most of the remaining stars to the survey in 2003 with the addition of the Carnegie 6.5-m Magellan II telescope. Butler's survey currently achieves a long-term precision of 3 m/s radial velocity, sufficient to make 4-σ detections of Solar System analogues (Jupiter-mass companions at 5 AU), and he is working to improve the precision to 2 m/s. By 2010, these surveys will provide a first planetary census of nearby stars, allow estimates of the frequency of Solar System analogues, and provide the target list for NASA's Terrestrial Planet Finder (TPF). Co-I Butler is also a member of the astrometric planet search team of NASA's Space Interferometry Mission (SIM), scheduled for launch in 2009. SIM is intended to be capable of detecting Earth-mass planets in Earth-like orbits around the closest solar-type stars.

In addition, Co-Is Boss and Weinberger will begin in 2003 a new ground-based astrometric planet search, using Carnegie's du Pont 2.5-m telescope in Chile. When equipped with a specially-designed astrometric camera, the du Pont is expected to be capable of astrometric accuracies on the order of 0.25 milliarcsecond, sufficient to allow the detection with a signal-to-noise ratio of 4 of a long-period Jupiter-like planet orbiting a solar-mass star 5 pc away. Such long-period Jupiters are thought to be signposts for the existence of Solar System analogues. Co-Is Boss and Weinberger will undertake this new effort as a part of the Carnegie NAI team.

Co-I Boss is a member of the Science Team for the Kepler Mission, a space telescope that will be capable of detecting the presence of hundreds of Earth-like planets in orbit around stars in the disk of our galaxy at the same galactic radius as the Sun. Kepler will detect these planets by the transit method, looking for dimming of starlight on the order of a part in 10,000. Kepler is scheduled for launch in 2007. Co-I Seager is using Carnegie's Las Campanas Observatory to search for extrasolar planets by the transit method. Ground-based transit surveys are capable of detecting the presence of Jupiter-sized planets in short-period orbits around solar-type stars (similar to the "hot Jupiter" orbiting the star HD209458) and even smaller-radius planets orbiting lower mass stars.

5.2.4 Characterizing extrasolar habitable planetary systems (Astrobiology Roadmap Objective 1.2)

Background. The relative abundances of the carbon compounds CO and CH_4 are potentially very useful temperature indicators for hot Jupiters (Seager et al. 2000). The hot Jupiters have effective temperatures of around 1000 K, resulting from their extremely close proximity to the parent stars — seven times closer to their stars than Mercury is to our Sun. Equilibrium calculations for model planetary atmospheres indicate that at these high temperatures and for atmospheres of roughly solar composition, CO should be much more abundant than CH_4, whereas at lower temperatures it should be the other way around. The temperature structure of hot Jupiter atmospheres is key to characterizing them — possible hot Jupiter models span a temperature range that includes dominance of either CH_4 or CO. To date extrasolar planet atmosphere models have assumed that thermodynamic equilibrium is achieved (Burrows et al. 2001). However, in brown dwarfs, objects with similar effective temperatures, CO and CH_4 are not in equilibrium, perhaps because of convective dredge-up from deep within their atmospheres. Photochemistry may also play a role in the atmospheres of hot Jupiters.

The fact that Jupiter is rich in elements heavier than H and He ("metal-rich") due to "pollution" by planetesimals shortly after its formation raises interesting questions for extrasolar giant planets. Are the extrasolar giant planets also metal-rich? Is their metallicity related to factors in their environment (such as number of giant planets in the system or metallicity of the parent star) that are also likely affected by planet formation? Because H_2O is expected to exist in vapor form at the temperature range of most of the known extrasolar giant planets, and because of its high abundance and strong absorption features, H_2O absorption bands should be among the easiest spectral features to detect in extrasolar giant planets.

Carbon dioxide is a good indicator for the presence of an atmosphere around terrestrial-sized planets because it is the only major atmospheric feature common to Earth, Mars, and Venus. Carbon dioxide is an atmospheric feature considered as essential for detection by TPF (e.g., Seager 2003). One good spectral region for such measurements is in the mid-IR, where the contrast between the central star and the planet is large, but for CO_2 the strongest thermal IR emission line is likely to be saturated. Thus, it could be used to determine if an atmosphere is present but little else. An alternative is to look for weaker CO_2 lines, potentially detectable with an alternative method: in transmission during a planet transit across the face of the star. As shown in Figure 5.2.2, Venus has many lines throughout the near-IR. Venus will transit the Sun in June 2004 for the first time in 120 years.

Research to Date. Co-I Seager is attempting to characterize the physical properties of extrasolar planets (spectra, density and temperature profiles). To do this Seager is developing radiative transfer models of extrasolar planet atmospheres (e.g., Seager et al. 2000). The results of such modeling will be used to interpret spectral data currently being acquired with ground-based telescopes and to be acquired in the next 5 years by space-based experiments. The aim is to determine the planets' atmospheric compositions and to also to predict their spectra for the design of future experiments (both from the ground and from future space telescopes).

Proposed Research. Co-I Seager proposes to develop kinetic models for the atmospheric chemistry that are necessary to explore quantitatively the potentials of CH_4 and CO as temperature indicators. The development of such models is well-suited for an NAI Postdoctoral Fellow. Seager also proposes to investigate the potential of H_2O and carbon-compound atmospheric features as diagnostics of planet metallicity, considering the likely observational parameters of proposed ground- and space-based search programs.

Finally, Seager proposes to model Venus' atmosphere in transmission (Figure 5.2.2) in order to use observations from the Venus transit as a test case for future extrasolar planet transit measurements (Seager & Sasselov 2000). The transit of Venus presents a unique opportunity for an NAI Postdoctoral Fellow to be trained in extrasolar planet atmosphere observations and theory, by participating in observations of the transit and in the data reduction and analysis.

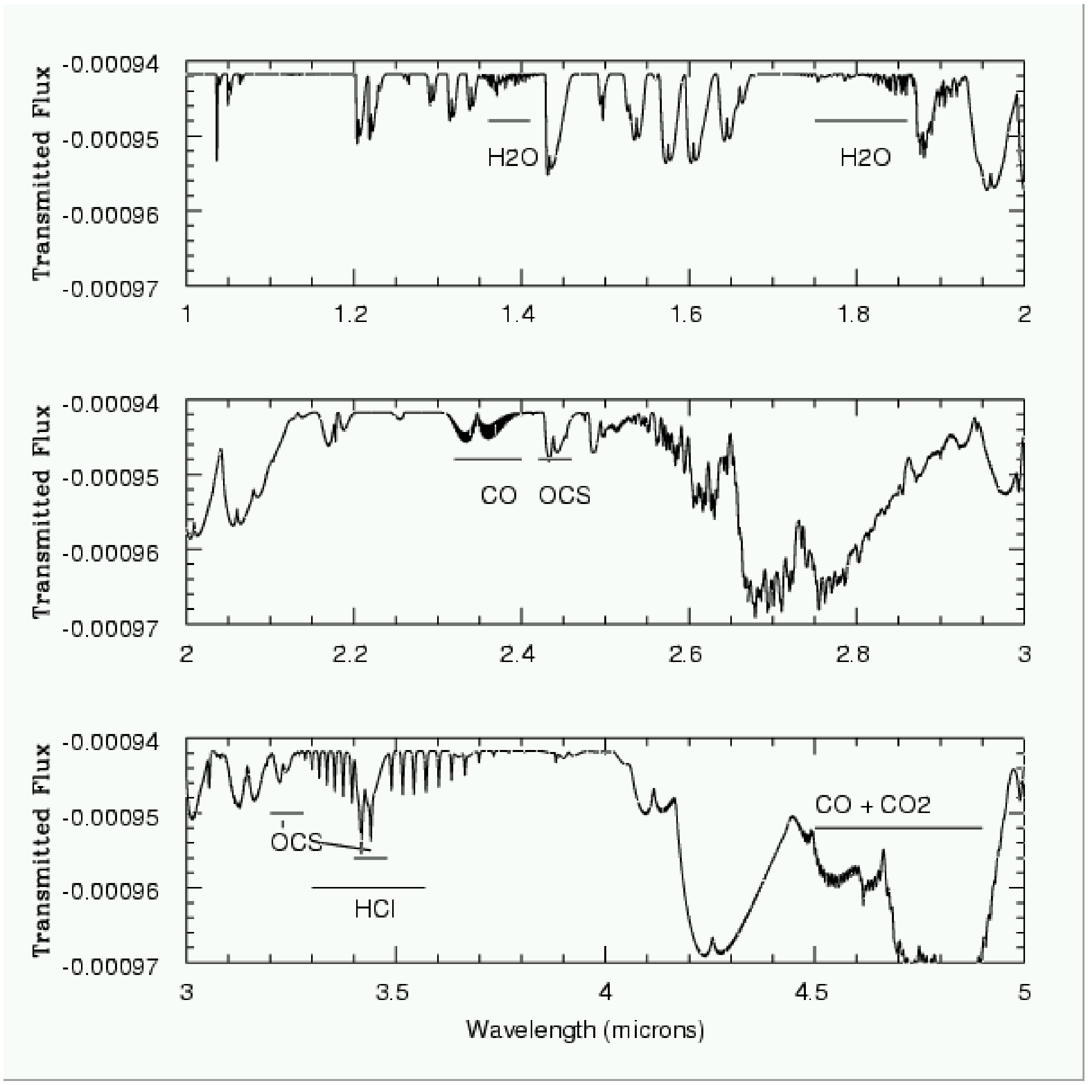

Figure 5.2.2. A model of the near-IR transmission spectrum of Venus at a spectral resolution of 10,000. The transmitted flux is the normalized in-transit minus out-of-transit flux, thus canceling out the stellar lines. Major absorption features are identified unless they are CO_2 features.

5.2.5 Habitable environments in the Solar System (Astrobiology Roadmap Objective 2.1)

Background. Much attention has been given to those few Solar System objects where the minimal conditions for life might all be present, including liquid water, essential chemical materials, and sources of energy. Early consideration of “habitable zones” in a planetary system where liquid water is stable at the surface of a planet under some atmospheric conditions has been modified by the realization that life might be possible in subterranean environments or within deep oceans overlain by thick shells of more or less permanent ice cover on outer planet satellites.

Research to Date. PI Solomon is supported by the NASA Planetary Geology and Geophysics Program to investigate aspects of the geological and geophysical evolution of solid planets and satellites. His recent work has focused on the thermal and magmatic evolution of such bodies, as well as the interaction between magmatism and atmospheric chemistry and climate. He is also a member of the Mars Orbiter Laser Altimeter team on the Mars Global Surveyor mission, and he has been using the highly precise new altimetric measurements to address problems ranging from interior processes to water-surface interactions on Mars. Among the results has been the demonstration (Phillips et al. 2001) that much of the volcanic construction and magmatic intrusion that created the Tharsis Rise on Mars occurred before the end of the Noachian epoch. This conclusion rests on the grounds that the global response to Tharsis loading influenced the downhill directions recorded by late Noachian valley networks. Another outcome has been the suggestion that the pattern of paleomagnetic anomalies may have been strongly influenced by hydrothermal alteration of magnetic carriers, following processes that occur in very young oceanic crust on Earth (Solomon et al. 2003).

Proposed Work. As part of his contribution to NAI research, Solomon will lead a task aimed at evaluating the locus, vigor, and history of hydrothermal activity that might have been possible or even favored within targeted settings in the modern Solar System and earlier in its history. That evaluation will be informed by considerations of heat sources versus depth and time as constrained by parameterized thermal histories and their dependence on internal volatile budgets (e.g., Hauck & Phillips 2002) as well as mechanical lithosphere estimates and other proxies for lithospheric heat flow (e.g., McGovern et al. 2002). Other considerations will include the sources and budgets of subsurface volatile inventories, the nature of rock compositions and fluid pathways (e.g., fault distributions, magnetic anomaly patterns on Mars), and constraints on compounds of carbon, nitrogen, phosphorus, sulfur, and other materials important for prebiotic organic chemistry. The findings from these evaluations will form a basis for the design of targeted experimental studies by other consortium members aimed at assessing the conditions for organic synthesis in possible hydrothermal systems on Mars, Europa, and other Solar System objects.

5.3 Extraterrestrial Materials: Origin and Evolution of Organic Matter and Water in the Solar System

What was the nature of the carbonaceous matter that was delivered to the early Earth and other planetary bodies? Meteorites and interplanetary dust particles (IDPs) provide information that is relevant to every stage of the processes that ultimately led to life in our Solar System. They also provide direct links among all aspects of this proposal.

Chondritic meteorites are primarily aggregates of material that formed in the solar nebula prior to or during the early stages of planet formation. Their asteroidal parent bodies are the last vestiges of the swarm of planetesimals from which the terrestrial planets ultimately formed. IDPs are thought to come from both asteroids and comets (Bradley et al. 1988). Many appear to have experienced less modification on their parent bodies than meteorites. They are in this sense more primitive than meteorites, but their size (10s of μm) makes their analysis more difficult.

Chondritic meteorites and IDPs also contain circumstellar and interstellar grains and interstellar organic matter that are a direct record of the prehistory of our Solar System (Messenger & Walker 1997; Bradley et al. 1999; Messenger et al. 2002). There is evidence that at least some fraction of the organic matter is a ubiquitous constituent of the interstellar medium (ISM) in our Galaxy and other galaxies (Pendleton et al. 1994; Pendleton & Chiar 1997). The bulk composition of the meteoritic material is also similar to the so-called CHON particles from comet Halley (Kissel & Krueger 1987). Meteorites and IDPs would have supplied a complex suite of organic matter to the terrestrial planets, including amino acids and nucleic acids (Cronin et al. 1988). The discovery that some amino acids in meteorites exhibit a slight "left-handedness" excess is particularly intriguing (Engel & Nagy 1982; Cronin & Pizzarello 1997; Pizzarello & Cronin 2000). If the enantiomeric excesses are in fact *bona fide* (i.e., not due to some contamination effect), then the chemistry that produced the organics in meteorites are our only example of a truly abiotic, chirally selective reaction pathway. Because of the enantiomeric excesses, some have even speculated that extraterrestrial organic matter played a direct role in the development of life on Earth (Pizzarello & Cronin 2000).

The presence of complex organic matter in chondritic meteorites and IDPs may also have played a second significant astrobiological role by modifying the Earth's early atmospheric composition. When micro-meteorites and IDPs are rapidly heated during atmospheric entry, organic matter is released pyrolytically (Kress et al. 2003). On the early Earth, the flux of exogenous material would have been high and the oxygen content of the atmosphere would have been low. As a result, this pyrolitic organic matter may have had a significant effect on its atmosphere by providing both greenhouse gases and UV-protective molecules such as PAHs (Kress et al. 2003).

Many chondritic meteorites experienced a period of hydrothermal activity that created a number of transition-metal sulfides and hydrated silicates. Some have suggested that similar minerals were essential for catalysis of prebiotic "metabolic" cycles on Earth (Wächtershäuser 1988; Russell & Hall 1997; Russell et al. 1998; Cody et al. 2001). One component of the organic matter in meteorites even forms vesicles that have been likened to primitive cell walls (Deamer & Pashley 1989; see **Section 5.5.1**). Given the abundance of complex organic matter and the presence of important catalysts, why did not life develop in meteorites? Time and pressure may have been two factors – the period of hydrothermal activity was probably quite short, and the small sizes of their parent bodies would have meant low pressures. In this regard, meteorites provide a natural model of a system clearly capable of promoting extensive organic chemistry, but probably incapable of bridging from pure chemistry to life.

The terrestrial planets were built up by accretion of many smaller bodies (Wetherill 1994b; Chambers & Wetherill 2001). Most of these objects would have undergone widespread partial melting and differentiation before being accreted. The fraction of the original carbon that would have survived this process and in what form it would have been preserved is not well understood. However, these questions are key to understanding the carbon budgets and degassing histories of the terrestrial planets.

Of all the planets other than Earth, Mars is perhaps the most likely to have developed life. It shows abundant evidence for the past activity of liquid water at its surface. There is tantalizing evidence from satellite imagery that near-surface liquid water persists at least intermittently to this day (Malin & Edgett 2000; Costard et al. 2002). Meteorites provide us with the only samples of Mars that we can study in the laboratory. All the Martian meteorites are igneous rocks, and many show evidence of having experienced aqueous alteration on Mars after crystallization (McSween & Treiman 1998). The crystallization ages of these meteorites provide upper limits for the ages of this alteration and indicate that aqueous activity on Mars has continued up until almost the present day – the youngest Martian meteorites are ~180 Ma old (McSween & Treiman 1998). Thus, meteorites also provide evidence of the nature of the sub-surface hydrosphere on Mars.

5.3.1 Organic carbon in meteorites and IDPs (Astrobiology Roadmap Objective 3.1)

Background: Organic carbon in meteorites. Through funding from NASA's Origins of Solar Systems Program, Co-Is Cody and Alexander have focused on determining the structure of meteoritic macromolecular organic matter, the dominant form of organic carbon, by solid-state nuclear magnetic resonance (NMR) spectroscopy (Cody et al. 2002, 2003a). These studies show that the meteoritic organic matter has an extremely complex distribution of C-bearing organic functional groups and exhibits enormous differences in the relative abundances of functional groups within and between chondritic classes. However, we do observe certain chemical similarities in all meteorites, suggesting a common precursor that has been variably modified by parent-body processes.

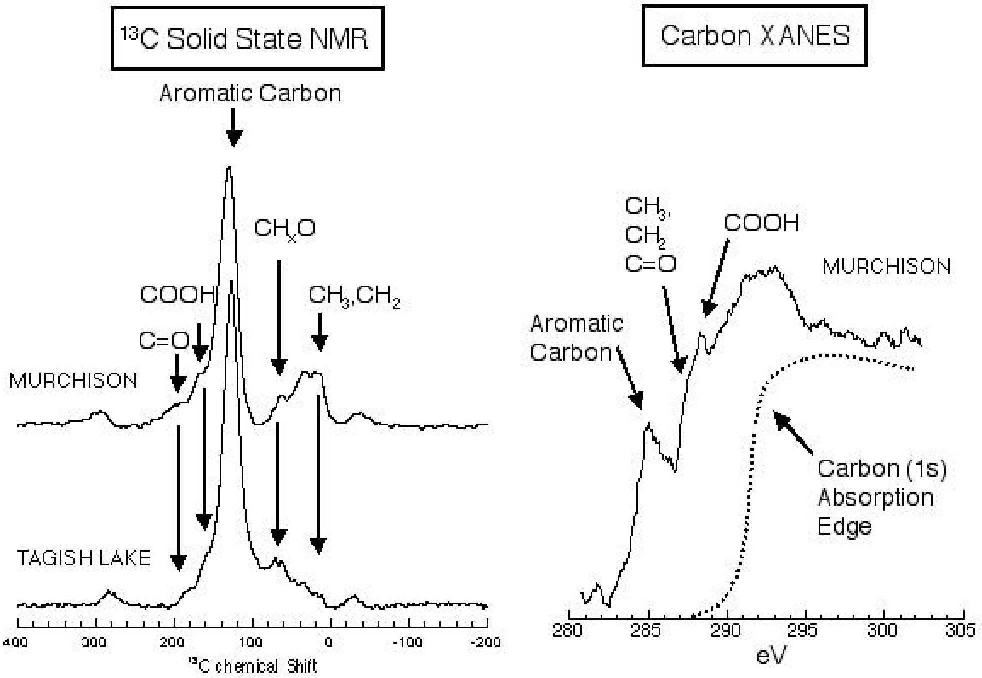

Figure 5.3.1. A comparison of the chemical information recorded by solid state ^{13}C nuclear magnetic resonance (NMR) spectroscopy vs. carbon (1s) X-ray Absorption Near Edge Spectroscopy (XANES). NMR spectra of the organic matter in the Murchison and Tagish Lake meteorites (left) reveal enormous chemical complexity in both samples while also exhibiting tremendous differences in the relative distributions of organic functional groups. C-XANES of Murchison records the same organic functionality in the pre-edge region of the spectrum. Note that C-XANES suffers from considerably greater band overlap compared with NMR. C-XANES, however, can be obtained on sub-femtogram quantities, whereas NMR requires sample weights in excess of ~ 20 mg (ideally 100 mg).

What is still needed, and cannot be done by NMR, are equally stringent constraints on N and S speciation. Pyrolysis gas chromatography/mass spectrometry (GC-MS) analyses do reveal both N- and S-containing organic moieties, but this technique may not be detecting all of the organic matter and the pyrolysis may modify the heteroatomic molecules from their pristine configurations.

The NMR and pyrolysis techniques are also relatively insensitive. We would like to obtain similarly detailed information from rare meteorites, IDPs, and cometary samples returned by NASA's Stardust mission. The H and N isotopic compositions of organic matter in IDPs exhibit a much wider range of compositions than in meteorites (Messenger 2000), suggesting that they have been less modified by parent-body processes. The organic matter in the Stardust samples is also likely to be very primitive, although possibly modified during collection. To analyze these materials, we need to develop new microanalytical techniques.

Proposed Research. Our NAI-specific work will focus on astrobiological and mission-related issues associated with the chemistry of chondritic organic matter. In particular, we will obtain high-quality information on the organic N, O, and S contained in meteoritic organic matter. High resolution X-ray Absorption Near Edge Spectroscopy (XANES) is probably the best means of obtaining this information, particularly for small samples (Figure 5.3.1). We specifically seek support for research at the Scanning Transmission X-ray Microscope (STXM) and microspectrometer at the Advanced Light Source (a 4.0-GeV synchrotron) at Lawrence Berkeley National Laboratory. Co-I Cody is a member of the principal research team for this instrument, and Collaborator Ade is the principal beamline scientist. We propose to use the STXM to acquire XANES spectra of meteoritic organic matter, exploiting the characteristic fine structure on the C(1s), N(1s), O(1s), and S(2p) absorption edges. Light-element XANES has been previously successfully applied to probe the electronic structure of organic carbon in terrestrial kerogenous materials (Cody et al. 1995a,b, 1996, 2000; Boyce et al. 2002) and has been shown to provide fairly well-resolved functional group information. C- and O-XANES has been recently applied to the study of IDPs and some meteorites (Flynn et al. 2001). The application of N, O, and S-XANES to our collection of meteorites will place constraints on perhaps the most interesting (in an astrobiological sense) of their exogenous organic compounds. We will use the XANES data, calibrated against various N, O, and S organic standards, to develop a consistent fitting scheme by which any exogenous organic solid can be analyzed and chemically characterized, even given femtogram quantities.

The application of C-XANES provides an equally useful function. We now have a thorough understanding of the carbon chemistry in meteoritic macromolecular material via solid-state NMR (Cody et al. 2002, 2003a). We will use these data to fit C-XANES spectra and obtain reasonable estimates of the critical optical parameters, i.e., the oscillator strengths associated with electronic transitions corresponding to various organic functional groups. It is important to be aware that organic functional groups detected with XANES (like IR spectroscopy and unlike NMR) may have vastly different molar absorptivities, thus some functional groups (e.g., COOH, and RCO) exhibit very strong absorption relative to other functional groups, e.g., CH_2 and CH_2O. Furthermore, C-XANES typically suffers from substantial band overlap (Figure 5.3.1), leading to complications in band assignments. Using our extensive NMR data to constrain the C-XANES data on meteorites will, therefore, provide an extremely valuable database that can be used to quantify the C chemistry within extremely small samples (e.g., IDPs), where the application of NMR is impossible. This database will be made available to the entire scientific community and thus will facilitate the quantitative analysis of any extraterrestrial organics.

Background: Organic Matter in IDPs. Interplanetary dust particles (IDPs), collected by aircraft in Earth's stratosphere, are believed to be among the most primitive extraterrestrial materials currently available for laboratory study (Bradley et al. 1987; Messenger 2000). These small (typically < 20 μm) particles are generally aggregates of much smaller grains of silicates, Fe-Ni metal, sulfides and carbonaceous material. They have bulk chemical compositions similar to carbonaceous chondrites but are more highly enriched in C. Laser-desorption mass spectrometry (Clemett et al. 1993), Fourier Transform Infrared (FTIR) spectroscopy (Flynn et al. 2002), and C- and O-XANES (Flynn et al. 2001) have all shown that much of the carbonaceous material is organic, rather than elemental C, bolstering the suggestion of Anders (1989) that IDPs could have been an important source of organic matter to the early Earth. Moreover, large and variable enrichments of D and ^{15}N (relative to H and ^{14}N and terrestrial ratios) in most cases appear to be associated with organic matter (Messenger 2000; Aléon et al. 2001), indicating preservation of organic material inherited from the presolar molecular cloud.

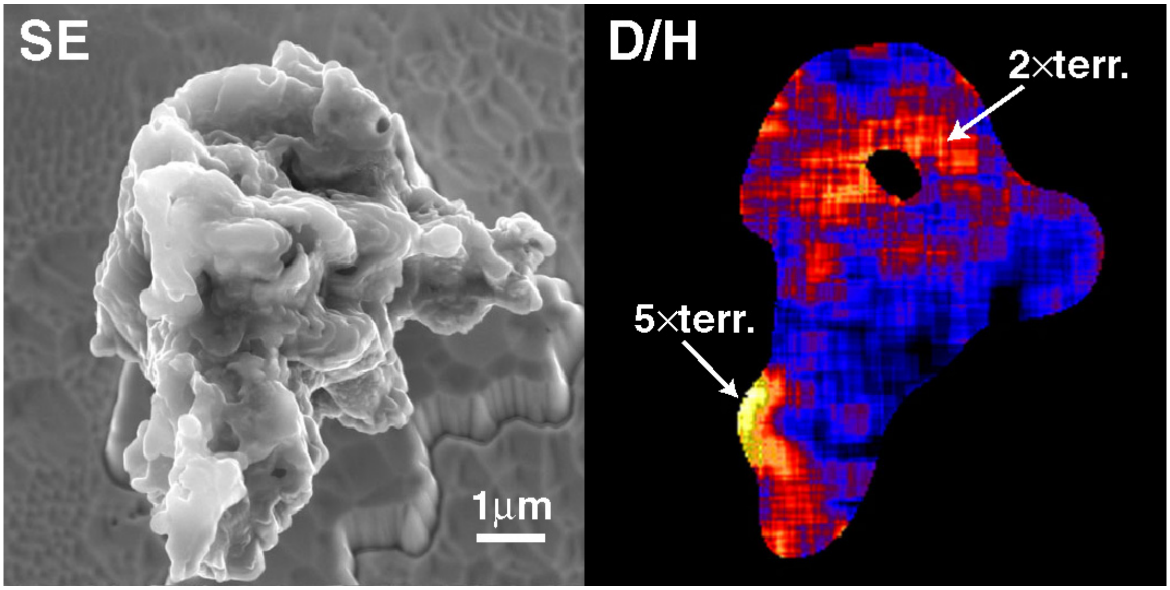

Figure 5.3.2. Images of a cluster interplanetary dust particle (IDP) fragment collected in the Earth's stratosphere. Left panel: secondary electron image. The IDP consists of carbonaceous material intermixed with fine-grained silicate and sulfide minerals. Right panel: Hydrogen isotope image of IDP generated by an ion microprobe. The D/H ratio is highly variable on a µm scale. D/H reaches 5 times the terrestrial value in the most carbonaceous region of the particle, indicating partial preservation of interstellar organic material.

Proposed Research. Co-Is Nittler, Alexander, Cody, Steele, and Stroud request support to characterize IDPs isotopically, chemically, and mineralogically on a micron and sub-micron spatial scale. The goals of the proposed research are to (1) characterize more completely the presolar molecular cloud matter preserved in the particles, (2) trace the alteration processes that have affected the organic matter, and (3) compare the IDP organic matter with that preserved in primitive meteorites. A multi-technique approach allows the most information to be obtained about the organic material in the IDPs (e.g., Keller et al. 2002). Isotopic imaging with the CIW ims-6f ion probe will be used to investigate quantitatively the spatial distribution of D/H, C/H, and $^{15}N/^{14}N$ ratios in IDPs with a ~1 µm spatial resolution (Nittler & Messenger 1998; Mukhopadhyay et al. 2002) (Figure 5.3.2). Several techniques will subsequently be used to characterize chemically and mineralogically the isotopically analyzed IDP material, including field-emission scanning electron microscopy, fluorescence microscopy (Co-I Steele), transmission electron microscopy (Co-I Stroud), and scanning transmission X-ray spectro-microscopy (STXM, Co-I Cody, see **Section 5.3.1**). The isotopic work is currently funded by a NASA grant to Co-I Nittler.

Transmission electron microscope (TEM) and STXM analyses require ultrathin (~100-nm) samples. These samples will be prepared either by ultramicrotoming of IDPs embedded in S (Keller et al. 2002) or by focused ion beam (FIB) techniques (e.g., Stroud et al. 2002). By tagging specific functional groups (e.g., PAHs amines) in these sections with fluorescent molecular probes, fluorescence microscopy can be used to characterize the spatial distribution of those groups (Clemett et al. 2002).

STXM can be used to obtain both elemental abundances and electronic structure information (e.g., bonding) with very high sensitivity (femtomole detection) and high spatial resolution. Co-Is Cody and Nittler will perform C-, N-, O- and S-XANES (see above) imaging of the IDPs. Previous XANES measurement of IDPs have indicated the presence of C=O double bonds and a much higher O/C ratio for IDP organics than seen in meteoritic organics (Flynn et al. 2001). Correlated isotopic and XANES measurements on the same material will allow us to search for correlations between type and abundance of chemical bonds and isotopic compositions. Complementary to the STXM analyses, Co-I Stroud will use TEM techniques to characterize the IDPs. High-resolution imaging, EDS analysis, and electron energy loss spectroscopy (EELS) imaging will be used to characterize silicate mineralogy, the chemical bonding environment, and speciation of organic C and N (Keller et al. 1997) and correlate these with isotopes. The IDP EELS spectra will also be compared with spectra from the well-characterized meteorite samples (see above).

5.3.2 The fate of carbon during planetary differentiation (Astrobiology Roadmap Objective 3.1)

Background. Carbon from the interstellar medium and the solar nebula is incorporated into chondritic meteorites, occurring in a variety of forms (amorphous organic carbon to ordered graphite) and with a wide range of isotopic signatures. While this material forms the reservoir of carbon assembled into planets and available for abiological and biological evolution, the planets themselves have undergone differentiation. Relatively little is known about the effect of planetary differentiation on carbon and its isotopic signatures. While we might expect planetary-scale differentiation at high temperatures to homogenize the isotopic signatures, we know relatively little about the time scales on which this happens or the ultimate fate of the incorporated carbon.

Proposed Research. Co-I McCoy, along with Postdoctoral Fellow C. M. Corrigan (Smithsonian), collaborator G. K. Benedix (Wash. Univ.), and Co-I Nittler, will investigate the mobilization and isotopic homogenization of chondritic carbon during partial melting and differentiation through both experimental melting of chondritic meteorites and analyses of carbon isotopic signatures in both these experiments and natural, partially-differentiated meteorites. In collaboration with Co-I Vicenzi, carbon in the experimental charges will be mapped at high spatial resolution (~0.25 μm) prior to isotopic analysis, using time-of-flight secondary ion mass spectrometry (ToF-SIMS). This characterization will reveal trace and free carbon, as well as potentially illustrating transport paths along grain interfaces that may otherwise go undetected using conventional X-ray microanalysis.

McCoy, Benedix, and Corrigan are currently undertaking a series of experiments to examine partial melting and melt migration in chondritic meteorites heated between 1000°C (just above the Fe,Ni-FeS cotectic) and 1300°C. These experiments should allow us to trace the movement of carbon during melting. Our expectation is that carbon is an early-melting phase that will concentrate in the Fe,Ni-FeS cotectic melt. During planetary differentiation, this outcome would result in most of the carbon being segregated into the core and removed from the zone of biologic activity. This conundrum between the requirement for carbon to initiate life and its expected behavior during melting is the driving force for these experiments.

The second phase of the work will involve analyses of carbon isotopic signatures. During the past 10 years, there has been a growing recognition that within the world's meteorite collections examples exist of the earliest stages of differentiation, arrested before reaching completion. Preliminary work by Co-Is McCoy and Nittler on one of these meteorites – lodranite GRA 95209 – suggests that carbon isotopic heterogeneity may be preserved during partial melting. Despite having reached temperatures that generated significant silicate partial melting (perhaps 1250°C), graphite rosettes contained within metal exhibit carbon isotopic signatures ranging from $\delta^{13}C=-55$ to $+75‰$. Furthermore, these isotopically diverse graphite rosettes often occur within a few tens of microns of one another. This pattern strongly suggests that the initial, chondritic isotopic heterogeneity was preserved, despite significant partial melting. Analyses of controlled melting experiments, as well as additional analyses of graphite-bearing stony-iron meteorites (e.g., particularly silicate-bearing IAB irons) should allow us to constrain further the extent of heating and melting required to produce isotopic homogeneity.

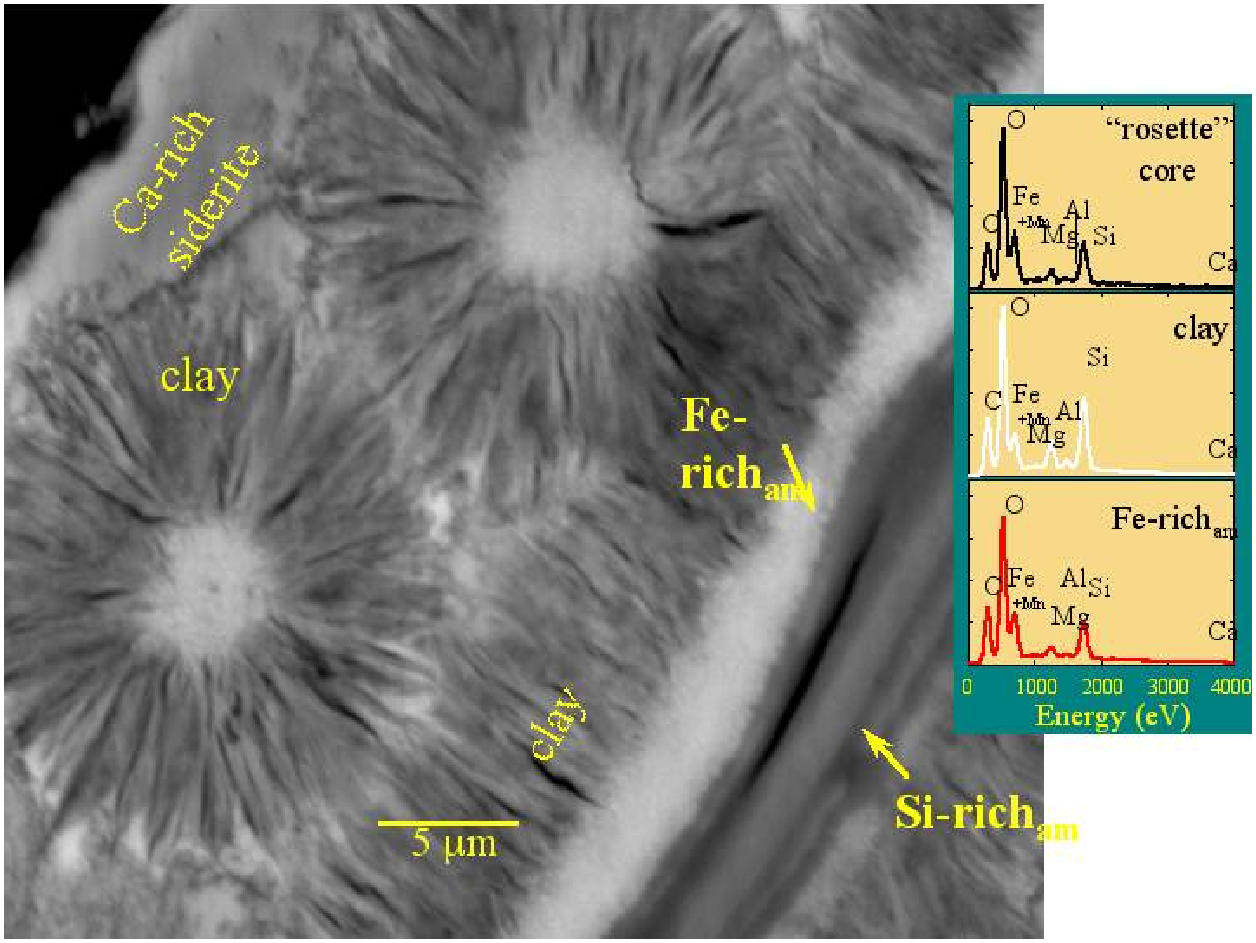

Figure 5.3.3. A backscattered electron image taken with a scanning electron microscope (SEM) of a fine-grained region of hydrothermal alteration of the Martian meteorite Lafayette. The insets are energy dispersive X-ray spectra of various regions. This particular region is dominated by clay minerals but includes Ca-rich siderite ($FeCO_3$) and a vein of iddingsite.

5.3.3 The Martian hydrosphere: Clues from meteorites (Astrobiology Roadmap Objective 2.1)

Background. A strong body of evidence exists for the claim that liquid water once was present on, or beneath, the surface of Mars. Large-scale (atmospheric observations/modeling) and regional-scale (surface morphologies) studies offer the opportunity to understand Mars as an evolving system. For instance, its now dry surface and the large D enrichment of its atmosphere suggest that most of Mars' atmospheric water has been lost to space. There are models for how this might have occurred. However, the most tangible evidence for the evolution of Mars comes from Martian meteorites. The Martian meteorites are all igneous rocks with crystallization age that range from 4.5 Ga to almost the present day. They include primary water-bearing minerals, shock-produced glasses, and secondary alteration minerals (Figure 5.3.3). The alteration minerals are presumably the products of processes occurring in Mars' subsurface hydrosphere. Thus, the meteorites potentially provide us with a record of the evolution of Mars throughout its history, particularly the history of its hydrospheric and atmospheric water (e.g., Leshin 2000). This information will help in assessing whether life could have evolved on Mars and where it might survive today.

Research to Date. We have determined the H isotopic compositions and water abundances of primary minerals and shock-produced glasses in 10 Martian meteorites (Boctor et al. 2003). The minerals and glass are generally enriched in D, probably because they have interacted with Martian hydrospheric and atmospheric water during the shock events that produced the glasses. A more direct record of the Martian hydrosphere is found in the alteration products in meteorites. The alteration products in some meteorites are only 100s of Ma old (e.g., Swindle et al. 2000), indicating that the Martian hydrosphere remains active, at least intermittently, to this day. The isotopic compositions of H (Karlsson et al. 1992; Eiler et al. 2002) and O (Farquhar & Thiemens 2000) in the alteration minerals, estimated by conventional extraction methods from bulk samples of the meteorites, strongly suggest a linkage between the atmosphere and hydrosphere of Mars. We intend to take advantage of microanalytical techniques to provide a better understanding of the physical and chemical conditions near the interface between subsurface fluids and the Martian atmosphere.

Proposed Research. Co-I Vicenzi will conduct a detailed examination of C-bearing and associated secondary minerals in Martian meteorites using high-spatial-resolution ToF-SIMS. The temperatures for such precipitation from fluids in the Martian crust are poorly constrained but have been estimated to be < 100°C to –30°C (Romanek et al. 1998; Treiman 1993), a range well within the window for life. At such low temperatures, reaction rates are sluggish, and many of the alteration phases have grain sizes on the micron to submicron length scales, and some silicates lack periodicity all together. The Ga ion source provides the spatial resolution (~0.1-0.3 μm) for studying the compositions of complex secondary assemblages through two-dimensional (2D) and shallow three-dimensional (3D) ion imaging.

The goal of these studies will be to (1) use the parallel detection capabilities of ToF-SIMS to determine the disposition and covariation of H, C, N, O, OH, P, S, and Cl in the alteration products, (2) use the high-resolution ion images to guide magnetic sector SIMS isotope analyses, e.g., D/H, $\delta^{13}C$, and $\delta^{18}O$ (conducted in conjunction with Co-Is Nittler and Alexander), (3) perform *in situ* focused ion beam (FIB) milling in the ToF-SIMS to obtain a quasi 3D view of structures and aqueous deposition boundaries noted in the high resolution ion images. Follow-up electron and low-energy X-ray imaging will be conducted with the analytical tools available on the Carnegie field-emission gun scanning electron microscope (FEG SEM) with Co-I Nittler.

5.4 Prebiotic Chemical and Isotopic Evolution on Earth

Did the emergence and sustenance of Earth's first life depend on unique attributes of Earth's earliest sulfur cycle? This question lies at the core of NASA-sponsored astrobiological research. A major component of the solution to this question hinges on a robust determination of the most probable initial planetary conditions, i.e. the chemical compositions of the early atmosphere, oceans, crust, and mantle, and fundamentally deducing the nature of the first geochemical cycles that couple these reservoirs. Knowledge of these cycles may provide a critical set of boundary conditions for establishing a probability for the emergence of life.

From our knowledge of Earth history it appears that life arose early and may likely have been an inevitable consequence of the initial geochemical evolution the planet. However, as a consequence of Earth's active tectonism, little record remains of the first 500-700 millions years of Earth history. What can be deduced is that Earth's earliest history began with the cataclysm of accretion (and possibly a massive Moon-forming impact event). The kinetic energy associated with Earth's formation (and the substantial impacts that followed shortly thereafter) was sufficient to vaporize much of the Earth and resulted in a magma ocean on the surface blanketed by a hot, dense atmosphere.

The sustained high temperatures associated with such a process were more than sufficient to convert any accreted organic molecules (i.e., those included in the chondritic sources) to their most thermodynamically stable light constituents, e.g., CO_2, CO, N_2, H_2, H_2O. Thus, at the very beginning it appears reasonable to assume that there existed no complex organic molecules within and on the surface of Earth. It may not have taken considerable time after these energetic events, however, for the first stable crust, atmosphere, and oceans to have formed (Sleep et al. 2000). Furthermore, there exists evidence that the first continents arose very early after crustal formation (Wilde et al. 2001; Mojzsis et al. 2001). The establishment of crust, ocean, and atmosphere inevitably initiated Earth's first geochemical cycles (e.g., carbon, sulfur, water, weathering) coupling the chemistry of these primary environments and reservoirs. The early dynamic chemical equilibrium across the primary reservoirs was, no doubt, subject to significant evolution by the addition of volatiles from the rapidly evolving mantle, atmospheric losses to space resulting from earliest photochemistry, as well as a continual rain of exogenous carbon from the slowly tailing remnants of the late heavy bombardment phase of the Solar System's history.

Within this chaotic and currently ill-defined world, life evidently arose by as yet unknown pre-biotic processes in an unknown environment. There remains considerable uncertainty regarding exactly how any organic chemistry intrinsic to a primitive terrestrial planet bridged into the initiation of an RNA world (Gilbert, 1985). It appears likely, however, that the probability of such chemistry occurring must have been inextricably bound to the nature of the Earth's earliest geochemical cycles. In the absence of favorable carbon, sulfur, and hydrologic cycles, the crucial first prebiotic stages may never have occurred, negating the possibility of the emergence of life. Given that the Earth is our only example of a planet where life began, understanding the early geochemistry of this planet is critical to understanding the probability for the emergence of life. What we learn about the Earth may provide critical guidance on the types of astrobiological instrumentation packages sent to other terrestrial planets (see **Section 5.8** for more discussion). The search for ancient life on other planets may well begin by establishing a robust determination of the earliest history of other potentially interesting terrestrial bodies, such as Mars (as discussed in **Section 5.2.5**), and comparing these with what was apparently sufficient for the emergence of life on the Earth.

With this in mind we propose a multidisciplinary approach toward understanding the early Archean sulfur cycle. Specifically, we aim to determine the biological and non-biological signatures within the sulfur isotopic record and use these data to place constraints on the early sulfur cycle which, due to a highly reducing atmosphere, was quite different from the latter half of Earth's history. We will further seek to determine whether there were particularly favorable attributes of the early Archean sulfur cycle that enhanced the quality of abiotic organic chemistry catalyzed by transition-metal sulfides that may have played a role in the emergence of life.

5.4.1 Unraveling Earth's early sulfur cycle (Astrobiology Roadmap Objective 4.1)

Background. Of the stable isotopic proxies for reconstructing ancient environments and detecting early life, sulfur isotope systematics stand above all others because they record not only metabolic processes but also the role of ultraviolet (UV) photolysis in atmospheric chemistry. Isotope analyses of sulfur-bearing minerals in ancient sedimentary rocks reveal that early microbial life had a strong preference for the lighter isotopes. In general, chemical reactions often exhibit mass-dependent fractionation wherein the slight differences in mass (e.g., 32, 33, and 34 in the case of sulfur) manifest small but significant differences in reaction rates. These differences lead either to enrichments or depletions in the heavier isotopes in the products of a given reaction. The measurement of large mass-dependent fractionations of sulfur isotopes (associated with sulfate reduction and sulfide disproportionation) in low-temperature geologic environments (under conditions where kinetics inhibit inorganic processes) is convincing evidence of microbial activity.

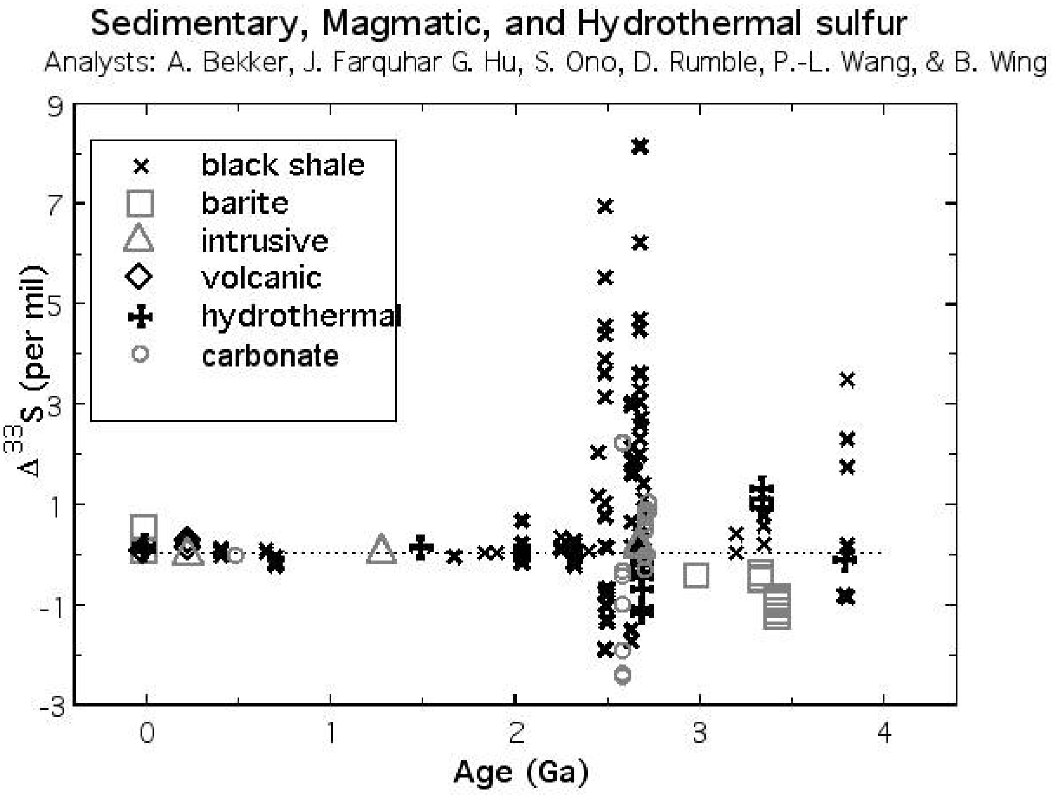

Figure 5.4.1. Values of •^{33}S (‰) for sedimentary, hydrothermal, and magmatic pyrite plotted versus age, where •^{33}S = δ^{33}S-0.515*δ^{34}S (‰). A •^{33}S (‰) near zero reveals mass-dependent fractionation, whereas deviation from •^{33}S (‰) ~ 0.0, in either a positive or negative sense, reveals mass-independent fractionation. Note the sharp break in distribution at an age of 2.3 Ga, the time proposed for the oxygenation of Earth's atmosphere. Before that time, values of •^{33}S range from -2.5 to 8 ‰; after 2.3 Ga, -0.5 < •^{33}S < 0.5.

Sulfur isotopes also exhibit the remarkable property of mass-independent fractionation (MIF). In the Earth's upper atmosphere today, certain gas-phase reactions promoted by solar UV light lead to fractionations of the various sulfur isotopes at variance with the typical mass-dependent fractionation line. There is not currently a very satisfying explanation for MIF phenomena; however, when such fractionation is observed it is invariably connected with photolytic gas-phase reactions (e.g., Farquhar et al. 2000).

These distinctive MIF fractionations are only rarely preserved at the Earth's surface, and then under unusual conditions. Polar ice cores, for example, contain sulfate aerosols derived from historic giant volcanic eruptions whose eruptive clouds reached into the stratosphere, penetrating the ozone shield (Savarino et al. 2002). These sulphates exhibit small but detectable mass-independent fractionations. Aerosol sulphates derived from smaller eruptions incapable of rising above the troposphere exhibit only mass-dependent fractionation. The modern stratigraphic record of sulphate derived from volcanogenic sources thus reveals predominantly zero MIF effects punctuated by spikes corresponding to particularly large volcanic events.

The widespread prevalence of MIF in sulfur isotopes in Archean sediments is in strong contrast to their limited distribution today (Farquhar et al. 2000; Ono et al. 2002) (Figure 5.4.1). Analysis of drill cores of black shale from Australia and South Africa over an age range from 2.5 to 2.7 Ga shows a continuous geologic record of atmospheric production of MIF sulfur further modified by microbial activity at the seawater-sediment interface during deposition and diagenesis (Ono et al. 2002). The disparity in stratigraphic distribution between present and Archean sediments demonstrates a modern, episodic versus an ancient, continuous production and preservation of MIF sulfur. These relationships reveal a profound difference between the atmosphere as we breathe it and the atmosphere that existed during the Archean.

Numerical simulations of modern atmospheric chemistry have been used to provide a comparison of hypothetical anoxic atmospheres, postulated to have existed in Archean times. It appears that the sulfur isotope MIF anomalies are unlikely to survive in the presence of oxygen. In an oxygenated atmosphere, both the products and reactants of photochemical reactions are eventually fully oxidized to sulfuric acid, resulting in mixing and elimination of the MIF signature induced during photolysis (Pavlov & Kasting 2002). Modern preservation in sulfate aerosols from giant volcanic eruptions demonstrates the necessity of immediately storing MIF sulfur in solid particles that are less vulnerable to oxidation and isotope exchange than gas molecules.

The preservation of MIF sulfur isotopic signatures in an anoxic Archean atmosphere was not as difficult. First, in the absence of atmospheric oxygen no ozone shield would have existed to prevent photolytic reactions occurring throughout the atmosphere. Consequently, a considerably larger fraction of the sulfur records the MIF signature (Farquhar et al. 2000). Second, the products of photochemical reactions were much less likely to be attacked by oxygen, thus preserving the sulfur species that carries the MIF signature. Model calculations (Pavlov & Kasting 2002) indicate that MIF fractionations would have been preserved in aerosol particles of elemental sulfur as well as in sulfate aerosols delivered to the hydrosphere. In the absence of oxidative weathering of continents, atmospheric sulfate aerosols would contribute a sulfur isotope MIF signature to seawater. The particles of elemental sulfur would likely accumulate in sediments and be utilized by microbes, perhaps leading to the precipitation of pyrite.

Although microbial activity will impart a distinct mass-dependent isotope fractionation signature through SO_4^{2-} reduction, the precursor MIF signatures will persist. Microbes catalytically promote the precipitation of insoluble sulfide minerals, thus storing the MIF signature in sulfide minerals such as pyrite. Different species of microorganisms utilize different forms of sulfur that carry different MIF signatures. For example, sulfate-reducing bacteria would lead to precipitation of pyrite with a seawater sulfate MIF. Microorganisms that reduce atmospheric elemental sulfur particles would lead to precipitation of pyrite with the MIF of the sulfur aerosols.

With extensive reworking, the metabolic activities of consortia of microorganisms may also obscure or even eliminate MIF sulfur isotopes. For example, poly-specific microbial communities typically recycle each others' waste products. If in a given environment a sulfur-oxidizing species used the sulfide produced by sulfur-reducers, the resulting sulfate would mix with seawater sulfate and the MIF signature would eventually be diluted to undetectible levels. Depending on the situation it is clear that microbes have the ability either to preserve or obscure the stratigraphic record of MIF. Thus, the magnitude of the MIF sulfur signature in ancient sediments reflects a fortuitous interplay between local environmental conditions, the ecology of microorganisms, and atmospheric deposition of aerosols.

Proposed Research. Co-I Rumble will lead four target investigations:

1. We plan to investigate in detail the stratigraphic record of the MIF signature in sulfur. We will seek to establish the pattern (or lack thereof) of geographic distribution in rocks of the same geologic age and measure highly resolved stratigraphic sections to investigate time-variation at specific geographic sites. We will focus attention on three critical time intervals, including:

2.5 to 2.0 Ga. We will analyze rocks that formed during this time interval to constrain, stratigraphically, when pO_2 level rose above 10^{-5} of present atmospheric levels, i.e., the point at which there was sufficient ozone to minimize the production of a strong MIF signature.

2.5 to 2.8 Ga. We will attempt to use both MIF and mass-dependent fractionation signatures to reconstruct the sulfur cycle in this transition period when O_2 photosynthesis first initiated (2.7 Ga or earlier) but while the atmosphere remained anoxic.

2.8 Ga to 3.5 (3.8?) Ga. We will seek isotopic evidence of the earliest sulfur-metabolizing organisms. This is an enormous challenge given the antiquity of this time interval, but progress may help provide the most robust signature of Earth's first life.

We will conduct fieldwork to collect suitable samples from each of the above time intervals from the relatively well-preserved Archean terrain exposed in Australia. Currently Co-I Rumble and collaborator Ono are actively participating in an Australian and international collaboration (including Johnson Space Center) to study this ancient terrain.

2. We will determine the extent to which the MIF signature is homogenous within a given stratigraphic unit. Toward this end, we will analyze individual pyrite crystals on a millimeter to micron scale with the new Thermo-Finnigan MAT 253 mass spectrometer in Co-I Rumble's laboratory at CIW. Our goal is to determine the degree to which sedimentary pyrite is homogeneous or heterogeneous isotopically. If given stratigraphic horizons are inhomogeneous, we may address whether this heterogeneity is due to microbial activity or to post-depositional metasomatism. Spatially resolved isotopic analyses will be crucial in answering these questions.

3. We will elucidate the mass-dependent microbial sulfur isotope signature through the analysis of controlled microbial cultures with Co-Is Emerson, Scott, and Steele. By measuring sulfur isotope fractionations by microorganisms, we will seek to apply laboratory fractionations to the interpretation of fractionations measured in Archean rocks. This research complements the goals outlined in **Section 5.7** of this proposal.

4. Technically we plan to develop new continuous-flow techniques for isotopic analysis of nanomole quantities of SF_6. Such new techniques will greatly aid the research described above. To accomplish our goals we will develop an ultralow-blank analytical protocol for the analysis of trace amounts of disseminated forms of sulfur in Archean sediments (and meteorites), including organic-bound sulfur, trace sulfate, and disseminated pyrite.

5.4.2 The critical role of sulfur in prebiotic (protometabolic) organic chemistry (Astrobiology Roadmap Objective 3.1)

Background. Over the past several decades our understanding of the diversity of habitats that support microbial communities has grown enormously. The recognition that life can exist even in some of the most inhospitable environments, e.g., the Antarctic dry valleys, has raised optimism regarding the slight possibility of extant life on other planets, most significantly Mars.

It is now apparent that virtually any environment that can be shown to provide biologically utilizable energy may sustain life. However, the range of environments suitable for the emergence of Earth's first life must have been much more restricted. Life could only have emerged in an environment capable of promoting the critical first organosynthetic reactions.

As it currently stands there is no satisfactory theory for the origin of life. A hypothetical, largely schematic, path from the initial abiotic world to Earth's first biology has been described as an ascendance through several key stages (e.g., de Duve 1991). In a condensed format, such a path starts with proto-metabolism, the stage where the natural environment promotes purely abiotic organosynthesis (i.e., abiotic carbon and nitrogen fixation). The consensus view holds that this protometabolic chemistry must have led into some manifestation of the "RNA" world (Gilbert 1985), the nascent stages of which involved spontaneous RNA replication. The ability to exploit crude molecular evolution was achieved at the point of primitive encapsulation (the first membrane, see **Section 5.5.1**). The development of RNA-dependent peptide synthesis, followed by the final development of translation, yields a first or "pre"-biotic system poised to intiate biological metabolism and herald in Earth's first life (de Duve 1991).

Research to Date. Although there has been substantial progress over the past three decades in research covering many of these path segments, for example in the area of RNA catalysis, there remains considerable uncertainty regarding how organic chemistry intrinsic to a primitive terrestrial planet bridged to the initiation of the RNA world. As part of our NAI research initiative, we have focused on the first stages (or the geochemical roots) of the origin of life, protometabolism. Our investigation has been and continues to be the experimental exploration of the importance of mineral catalysis (in particular transition-metal sulfides) in promoting the protometabolic stages of the origin of life.

One of the key aspects to deducing the prebiotic chemical origins of life on Earth, as well as constraining the potential for life on any other terrestrial planet (e.g., Mars), involves establishing where in either the atmosphere, oceans, or crust, natural geochemical cycling provided the most useful chemistry for pre-biotic biosynthesis. Our experiments have demonstrated the importance of sulfur (both inorganic, e.g., transition-metal sulifde, and organic, e.g., thiol) as an essential component for useful protometabolic chemistry. Certain organo-sulfur species, thioesters in particular, have long been proposed as particularly useful prebiotic intermediates, based on their large free energies of formation and their role in promoting organic chemistry that can provide the function and utility necessary to initiate anabolic biosynthesis (e.g., de Duve 1991; Wächtershaüser 1988). Their high energy content means that once formed thioesters can be used in organic reactions to drive otherwise endergonic reactions, e.g., the peptidization of amino acids. Acetyl-CoA is the ubiquitous thioester employed in many of the metabolic strategies of extant microorganisms. Both Acetyl-CoA and pyruvic acid are synthesized *de novo* by anaerobic chemoautotrophic prokaryotes (e.g., methanogens and acetogens) through the action of a complex set of enyzmes that contain within their active centers Fe and Ni (and possibly Cu, e.g., Doukov et al. 2002) sulfur clusters (Lindahl et al. 1990).

To date, the only demonstrated abiotic means for the synthesis of thioesters (relevant to the early Earth) has utilized transition-metal sulfides (e.g., Huber & Wächtershaüser 1997; Cody et al. 2003b). It may very well be that the essential prebiotic chemistry that led to the emergence of the phenomenon of life was inextricably bound to the presence of transition-metal sulfides. In addition to catalysts, however, the protometabolic environment also required a reliable source of energy and essential chemical substrates. This means that if life derived from endogenous chemistry intrinsic to the early Earth, the environment must have provided both readily available energy and light-element substrates (e.g., CO_2, NH_3, and H_2S), as well as natural catalysts to couple the energy and the chemical substrates to form biochemically useful molecules. Certainly, the most obvious energy sources are solar UV and visible radiation and thermochemical energy derived from redox disequilibria. Photo-driven prebiotic organic chemistry would necessarily have been restricted to the atmosphere, shallow ocean, and continental surfaces. Thermochemical energy could have been available wherever mixing of reduced and oxidized species result in thermodynamic disequilibria (e.g., Shock et al. 1996).

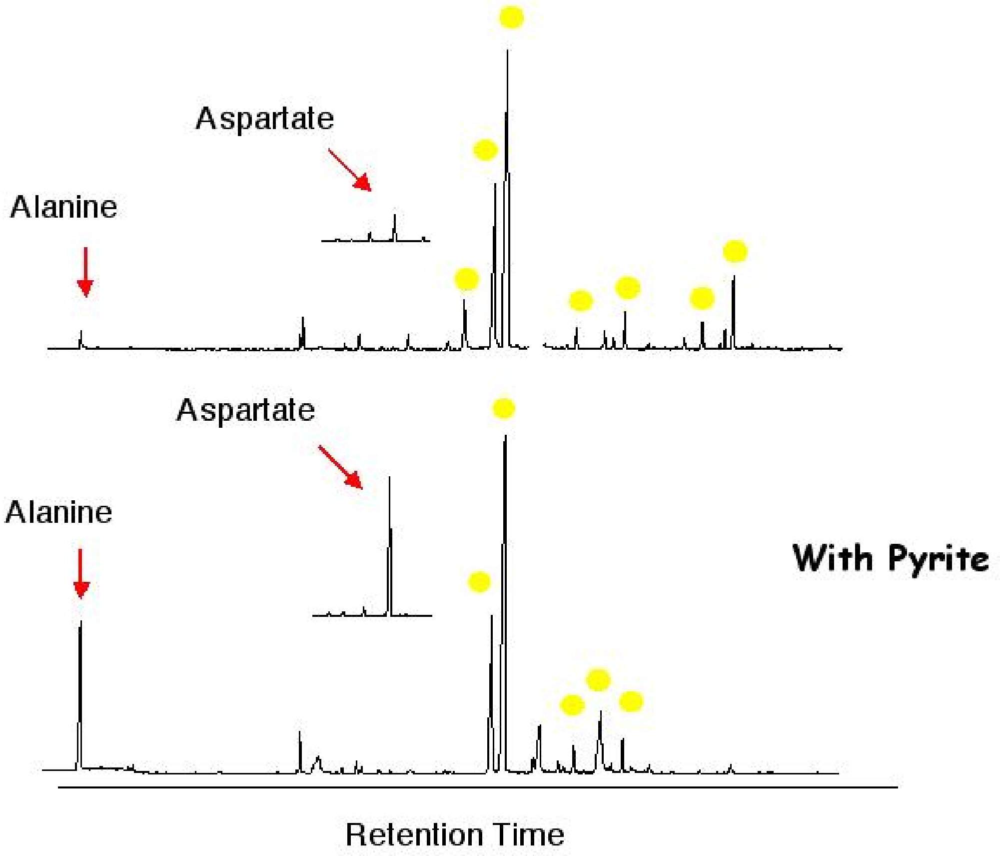

Figure 5.4.2. Chromatograms revealing the products of reactions of aqueous citric acid (100 mM) in the presence of 100 mM of ammonium formate run at 200 °C for 3 hours with and without pyrite. Of primary interest to protometabolic chemistry are the products of aqua-thermal decomposition of citric acid ending with the formation pyruvic acid (Cody et al. 2001). This reaction pathway presumably passes through the production of oxalacetic acid, although none of this important metabolic intermediate has been detected. In the presence of ammonium formate, a substantial quantity of pyruvate is converted to alanine through a reductive amination reaction. Small, but detectable, quantities of aspartic acid formed from the reductive amination of oxalacetic acid are also detected (shown here as an inset). The direct synthesis of aspartic acid (aspartate at this pH) is significant, as it mimics several key steps that occur in certain metabolic strategies. Aspartate also provides a critical threshold for the potential synthesis of pyrimidines, possibly connecting this hydrothermal chemistry with the roots of some type of RNA world. The presence of pyrite enhances the reductive amination, presumably by providing a catalytic site for the reduction of the imine intermediate.

Our previous work in this area has demonstrated the utility of a broad range of metal sulfide catalysts for the promotion of chemistry that bears (at least superficial) similarity with extant anabolic strategies of certain chemoautrophic anaerobic organisms (e.g., methanogens and acetogens). We have shown by experimental assay that many different transition-metal sulfides provide the catalytic qualities to promote protometabolically useful carbon fixation chemistry that largely mimics the Acetyl-CoA pathway utilized by both methanogens and acetogen as their primary carbon fixation and root anabolic pathway (Cody et al. 2003b). We have shown that transition-metal sulfides catalyze the reduction of nitrate and nitrite (potentially derived photochemically) (Brandes et al. 2000). We have identified, and provided supporting experimental results for, a plausible protometabolic carbon fixation pathway that uses transition-metal sulfides as heterocatalysts (Cody et al. 2001).

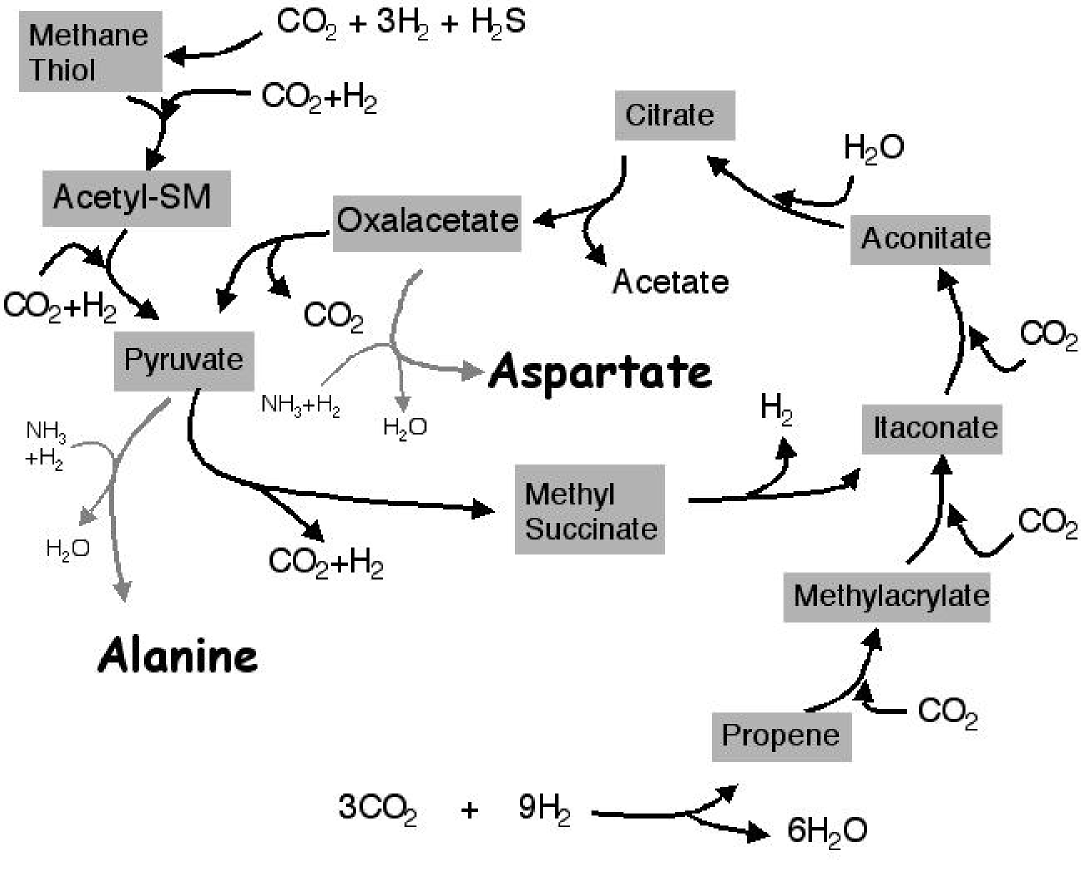

Figure 5.4.3. A composite of various *abiotic* ("protometabolic") carbon- (and nitrogen-) fixation reactions promoted or catalyzed in the presence of transition-metal sulfides and in aqueous media. This reaction network shares superficial similarities with intermediate anabolic strategies of certain anaerobic autotrophs, e.g., methanogens and acetogens. A reaction network such as this may have provided the primitive world with the essential biochemicals necessary to "jump start" an emergent chemical system, e.g., RNA world. The apparent complexity shown in this diagram does not, by any means, reflect a limit for abiotic chemistry; rather it records what has been observed to date in a very limited reaction space explored by relatively few researchers in experimental protometabolic chemistry (e.g., Heinen & Lauwers 1996; Huber & Wächtershäuser 1997, 1998; Cody et al. 2000, 2001, 2003a,b).

Recently, we have shown that we can couple nitrogen fixation for the promotion of amino-acid synthesis by utilizing segments of the above-mentioned protometabolic cycle, again in the presence of transition-metal sulfides. Specifically, we have shown that we can synthesize aspartate and alanine directly from citric acid under reducing conditions, with the reaction enhanced by presence of transition-metal sulfides (Cody et al. 2003c) (Figure 5.4.2). The hydrothermal synthesis of alanine has been demonstrated previously (e.g., Hafenbradl et al.

1995; Weber 1998, 2001; Brandes et al. 2000). The synthesis of aspartate is extremely important, as it may provide the critical bridge for the synthesis of certain nucleic acid bases, in particular the pyrimidine, orotic acid, the precursor to uracil, cytosine, and thymine (e.g., Abeles et al. 1992). Finally, we have shown that certain transition-metal sulfides will participate in reactions beyond just that of catalysts, yielding soluble organometallic iron-sulfur clusters that are capable of promoting the synthesis of alpha-keto acids from alkane thiol precursors (Cody et al. 2000). Figure 5.4.3 summarizes the results of our experiments, including those of others where transition-metal sulfides were used to promote reaction (e.g., Heinen & Lauers 1996; Huber & Wächtershäser 1997), placing the results in the context of a potentially useful protometabolic scheme for carbon and nitrogen fixation.

It must be stressed that the our experiments are <u>not</u> designed to explore directly the origins of life; rather they were designed and optimized to explore the ability of metal sulfides to promote "proto-metabolic" chemistry with possible relevance to the origins of life. Therefore, our previous results and the experiments proposed below should <u>not</u> be misinterpreted as supporting the possibility that life could have arisen at temperatures as high as 250° C.

Many important biomolecules are thermally unstable in aqueous media; for instance, functionalized sugars (both aminated and phosphorylated), peptides, polyphosphates, or thioesters will not survive long in water under hot hydrothermal conditions (e.g., Larralde et al. 1995; Shapiro 1995). Nitriles, such as cyanoacetylene and cyanoacetaldeyde — proposed as possible prebiotic precursors for pyrimidines (Robertson & Miller 1995) — will be rapidly hydrolyzed to carboxylic acids in hot water (Siskin et al. 1990). Therefore, if the synthesis of nucleotides and their subsequent oligomerization to promote an "RNA" world is requisite to the emergence of life, then such chemistry would be extremely improbable (and likely impossible) in high-temperature water (e.g., Miller & Lazcano 1995).

Nevertheless, in a pre-enzymatic "protometabolic" world, mineral catalysts were undoubtedly required to initiate a broad range of organosynthetic reactions for producing the first biomolecules. For at least some of this chemistry, it is difficult to conceive of better, naturally occurring, prebiotic catalysts than metal sulfides (e.g., the theories of Wächterhäuser 1988; Russell & Hall 1997; Russell et al. 1998). The challenge remains to demonstrate which catalysts did what and where the prebiotic chemistry ultimately converged into the phenomenon of life itself. The results of our previous experiments suggest that cool environments in close proximity to metal sulfide-precipitating hydrothermal hot-springs may have been advantageous to the emergence of life on the early Earth, as well as other terrestrial planets, such as early Mars or early Venus.

Proposed Research. To further our contribution to the prebiotic components of astrobiological research, Co-Is Brandes, Cody, Fogel, Hazen, Yoder and Collaborators Boctor and Sharma propose to continue and expand on our experimental studies of organosynthetic reactions that may have actually occurred on the Hadean and early Archaen Earth. Our focus in the CIW NAI team will be to provide a robust experimental assessment of the feasibility of such prebiotic chemistry on any terrestrial planet with an active sulfur cycle and volcanism to provide both reduced fluids and catalytically active metal-sulfide substrates. We propose the following:

Over the next cycle of research, Co-Is Cody, Brandes, Hazen, and Collaborators Boctor and Sharma propose to assess experimentally (quantitatively) the kinetics of key carbon-, nitrogen-, and sulfur-fixing reactions by focusing on establishing the dependence of temperature, substrate activities, fluid pH, and choice of catalytic substrate on the reaction rates. We have already shown what is possible under ideal, assay conditions; we now want to establish the key kinetic parameters that would allow for a robust global and historic assessment of abiotic synthesis in the early Archean. These experiments will utilize synthetic sulfides (prepared by Co-I Boctor) spanning geologically relevant compositional series (e.g., Ni^{2+} and Co^{2+} substitution in FeS and

FeS_2). Following these experiments, we will select from our extensive library of well-characterized natural specimens for a comparative analysis. Our assessment of the organosynthetic reaction rates and reaction pathways also has direct relevance for the proposed research outlined in **Section 5.6.1** on hydrothermal vent environments.

Co-Is Cody and Fogel will explore whether kinetic isotopic fractionation associated with the key organosynthetic reactions can serve as a definitive signature for protometabolic organosynthesis utilizing compound-specific gas chromatography isotope-ratio mass spectrometry (GC-IRMS) focusing initially on carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$). Such isotope fractionation has been shown to be the case for simple hydrocarbons, e.g., methane through butane (Sherwood Lollar et al. 2002). We will expand these analyses to organic chemistry that yields more complex (hence prebiotically more interesting) organic molecules, e.g., amino acids and various metabolic intermediates. In this regard, this research dovetails with the work proposed in **Section 5.7.1** on biosignatures. Kinetic isotope fractionation will be used to help constrain reaction mechanism, as well as allow us to determine whether one can distinguish between biological and abiological synthesis of biologically relevant molecules (e.g., amino and fatty acids). As part of the overall goal of employing sulfur isotope signatures to help constrain the global sulfur cycles, we will work with Co-Is Rumble and Farquhar and Collaborator Ono to develop methods for the analysis of sulfur isotopes in organosulfur-containing species.

Co-I Cody and Collaborator Boctor propose to explore catalytic organosynthetic reactions utilizing natural metal sulfide assemblages. Throughout most of our previous studies we have utilized laboratory-synthesized pure metal sulfide phases as a means of adding a degree of chemical control to what are otherwise complex reaction systems. Natural sulfide deposits typically contain multiple phases, e.g., coexisting sphalerite (ZnS), chalcopyrite ($CuFeS_2$), pyrrhotite ($Fe_{1-x}S$), and pyrite (FeS_2). Individual (natural) metal-sulfide phases are virtually never compositionally pure. Considerable cation substitution (iron for zinc, cobalt or nickel for iron) can occur in many of the predominant phases in natural sulfide deposits. Such substitutions will likely effect significant changes in the catalytic properties of a given metal sulfide phase. We anticipate that the naturally occurring transition-metal sulfide samples may reveal interesting synergetic effects and perhaps considerably enhance catalytic promotion of useful protometabolic reactions.

We will focus initially on two types of metal-sulfide-rich samples. The first are recent samples obtained from mineralized vent chimney-wall material provided by Co-I Baross. These samples tend to grade in their mineral chemistry and assemblages across the vent chimney walls, recording a range of precipitation temperatures (Tivey 1995). Co-I Baross has proposed (see **Section 5.6.1**) that certain extremophilic microorganisms that currently live within the porous vent chimney walls may exploit the natural catalytic qualities of transition-metal sulfides in their environment for the production of simple organic substrates to support heterotrophy. We will assay the catalytic or otherwise promoting qualities of these natural sulfides under conditions that mimic those in proximity to an active vent chimney to help test this hypothesis.

We will also investigate organosynthesis promoted by metal sulfides present in natural ore samples obtained from ancient massive sulfide deposits (e.g., the ~ 3.2-Ga Sulfur Springs VMS deposits of Western Australia; these sulfides are currently being studied by Co-I Rumble and Collaborator Ono in collaboration with Australian and international scientists; see **Section 5.4.1**). In both cases, we will use similar assaying strategies that were previously developed by us (Cody et al. 2003b) for the analysis of pure transition-metal sulfides. We will utilize isotopically enriched (^{13}C) reagents so that we will be able to separate our reaction products from any naturally present organic compounds (T. McCollum, pers. comm., 2003).

Finally, Co-Is Brandes, Cody, Hazen, and Yoder propose to conduct a series of experiments to establish whether there exist abiotic isotopic signatures for small molecule production and destruction in hydrothermal (and perhaps other) systems. Previous work has shown that in addition to potentially useful protometabolic chemistry, transition-metal sulfides also serve as powerful promoters of NO_x reduction and to a lesser extent N_2 reduction (Brandes et al. 1998, 2000, 2001; Schoonen & Xu 2001). Specifically, we propose to establish the isotopic fractionation factors for the production of methane and C_2-C_5 hydrocarbon gases from the reduction of CO_2 to compare with the natural occurrences of such gases where abiotic synthesis has been indicated (e.g., Sherwood Lollar et al. 2002) (see also **Section 5.7.2**). We will also establish isotope fractionation signatures among nitrogen species (NO, N_2O, N_2) produced during the transition-metal-sulfide-promoted reduction of NO_2 under strictly abiotic conditions. Our proposed experiments will seek to detect specific isotopic fractionation patterns based on the nature of the catalyst and reaction conditions. The proposed work aims to provide isotopic constraints to the interpretation of stable isotopic signatures of carbon and nitrogen that may be analyzed on future Mars lander missions that sample the regolith or polar ice. The reactions will be performed by Co-Is Cody, Hazen, and Yoder at CIW and the products analyzed at the Stable Isotope Laboratory at the University of Texas at Austin by Co-I Brandes.

5.5 Prebiotic Molecular Selection and Organization

By what mechanisms were biomolecules selected, concentrated and organized from the diverse prebiotic organic inventory? Many processes contributed to the synthesis and accumulation of organic molecules on the prebiotic Earth (e.g., Chyba & Sagan 1992). Synthesis in interstellar dense molecular clouds (Bernstein et al. 1995, 2002), in the primitive atmosphere (Miller 1953; Miller & Urey 1959), in hydrothermal systems (see **Section 5.4.2**) (Huber & Wächtershäuser 1997; Cody et al. 2000, 2001, 2003b), during impacts (Blank et al. 2001), in aerosols (Dobson et al. 2000; Tuck 2002), and perhaps even in igneous rocks (Freund et al. 2001) provided the primordial Earth with a diverse suite of organic molecules. Our proposed studies on prebiotic chemical and isotopic evolution on Earth (see **Section 5.4.2**) will amplify our understanding of these ubiquitous processes.

Notwithstanding the relatively facile prebiotic synthetic chemistry and accumulation of exogenous organic molecules near Earth's surface, there remains the significant challenge of understanding the origin of life. Life's molecular building blocks, unlike the diverse prebiotic inventory, are highly selected and are organized into functional macromolecules. Biological amino acids, sugars, lipids, and the metabolic intermediates epitomize this point. Terrestrial life relies predominantly on a suite of 20 different α-H levose (L) amino acids that are condensed to form proteins. By contrast, prebiotic processes produce a more diverse suite of racemic amino acids, which do not tend to form peptide bonds in most prebiotic environments. For example, the Murchison meteorite yields more than 70 different amino acids monomers, including α-methyl amino acids and β-amino acids not used in extent organisms (Kvenvolden et al. 1970). Extant life also uses enantiomerically pure pentose sugars, D-ribose and D-deoxyribose. While several studies demonstrate facile prebiotic synthesis of sugars via the formose reaction (Shapiro 1988; Weber 2001), such processes invariably lead to a complex suite of energetically similar molecules, including the eight chiral isomers of D-ribose, plus a variety of straight, branched, and cyclic tetroses, pentoses, and hexoses. In these and many other examples, extent life employs specialized synthesis pathways to achieve a high degree of molecular selectivity and macromolecular organization. The natural origin of homochirality in both monomers and biopolymers remains a mystery.

In this section we examine processes that might have promoted the selection and organization of prebiotically derived organic molecules into functional structures beneficial to emergent life. We propose to study two possible mechanisms: (1) the self-organization of amphiphilic molecules to form membrane-like bilayers in saline and non-saline aqueous solutions, and (2) the chiral selective adsorption and polymerization of amino acids and sugars on mineral surfaces.

5.5.1 Self-organization of amphiphiles (Astrobiology Roadmap Objective 3.2)

Background. Molecular self-assembly provides a potential solution to the problem of molecular selection and organization. In fact, self-assembly still plays a central role in life processes such as duplex DNA assembly from single complementary strands, protein folding, and membrane formation. Living cells are separated from their environment by membrane boundary structures that incorporate a lipid bilayer composed of amphiphilic molecules such as phospholipids and cholesterol. It is a simple exercise to show that vesicles composed of amphiphilic compounds (liposomes) spontaneously appear by self-assembly when amphiphilic molecules are introduced into aqueous phases (Bangham et al. 1965). It has been argued that such vesicles may provide reasonable models for the first membranous structures on the early Earth (Deamer 1997; Segré et al. 2001; Luisi 1996; Deamer et al. 2003).

Phospholipids will readily self-assemble into membranous vesicles. Membranous structures can also be prepared from single-chain amphiphiles such as fatty acids, fatty alcohols, and monoglycerides. Such vesicles may provide models for the formation of the earliest cellular compartments. The prebiotic early Earth would have provided multiple sources for such molecules (see **Sections 5.3.1, 5.3.2**, and **5.4.2**). For instance, carbonaceous meteorites contain a rich mixture of organic compounds that were synthesized abiotically in the presolar molecular cloud and in the early Solar System. Co-I Deamer and colleagues have established that certain components of the Murchison organics operate as surface-active amphiphiles and have been shown to assemble into membranous vesicles (Deamer 1985; Deamer & Pashley 1989) (Figure 5.5.1). Although the composition of the membrane-forming amphiphiles present in the Murchison organic mixture has not yet been established in detail, it is clear that monocarboxylic acids are present (Lawless & Yuen 1979; Shimoyama et al. 1989; Mautner et al. 1997). Monocarboxylic acids have also been synthesized under a variety of simulated prebiotic conditions (Huber & Wächtershäuser 1997; McCollom et al. 1999; Rushdi & Simoneit 2001; Dworkin et al. 2001; Cody et al. 2001, 2003b).

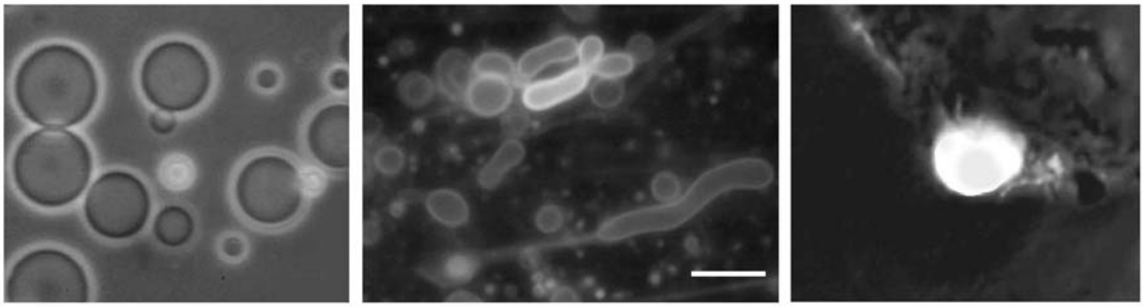

Figure 5.5.1. Membranous vesicles self-assemble from a variety of organic amphiphiles. Left: Murchison meteorite extracts contain amphihilic compounds that readily form membranes that are true permeability barriers to the flux of polar and ionic solutes. Center: Decanoic acid, a component of meteoritic organics, is one of the simplest amphiphilic compounds that can form stable vesicles. Right: Photoproduct from laboratory simulation of interstellar grain mantle ices (Dworkin et al. 2001). The photoproduct vesicle has captured pyranine, a fluorescent dye, which indicates the presence of a boundary membrane. The scale bar is 10 µm.

Research to Date. We have begun to investigate the physical properties of self-assembled structures produced by monocarboxylic acids of various chain lengths and of mixtures with other simple amphiphilic compounds. The bilayer-forming potential of fatty acids with shorter hydrocarbon chains (C8-C11) has been previously investigated (Hargreaves & Deamer 1978; Walde et al. 1994; Apel et al. 2002; Monnard et al. 2002). The length and the degree of unsaturation of the hydrocarbon chains play important roles in bilayer-membrane properties such as permeability and stability, which would have been determining factors for primitive life forms.

In spite of our ability to demonstrate facile vesicle formation using pure fatty acids (Deamer & Barchfield 1982; Deamer & Pashley 1989), we have discovered significant limitations of this model system. The primary problem arises because fatty-acid bilayer membranes are stabilized by van der Waals interactions between their hydrocarbon chains and by hydrogen bonds formed between deprotonated and protonated acid molecules. Therefore, formation of bilayer vesicles is extremely sensitive to the pH of the medium. We have found that such vesicles are stable only at pH ranges at or near the pKa of the fatty acid, i.e., over a very narrow pH range. We have also discovered that stability is a strong function of chain length, and at least 10-carbon chains are required for reasonably stable vesicles. The Murchison meteorite contains fatty acids with hydrocarbon chain lengths from C8-C12, while reaction products of prebiotic Fischer-Tropsch type synthesis also produce fatty acids with hydrocarbon chains in the heptanoic, octanoic, and nonanoic acids (Rushdi & Simoneit 2001).

The stability and permeability of fatty acid vesicles is dependent on bilayer-intrinsic physical properties and environmental conditions, including the salinity or the ionic strength of the bulk aqueous phase. For example, if the emergence of life took place in a marine environment, sodium chloride in solution would have exerted osmotic pressure across membranes, and it has been established that fatty acid vesicles cannot withstand sodium chloride concentration in the range of today's oceans (Monnard et al. 2002). Furthermore, the presence of divalent cations in marine salts, probably at concentrations in the range of several millimolar or higher, causes fatty acid vesicles to precipitate (the "hard water" effect, Monnard et al. 2002). Thus, the presence of divalent cations in the primordial aqueous environments would have severely inhibited the self-assembly of simple fatty acid vesicles.

A possible solution to this conundrum is that early membranes were not composed of pure fatty acids, but were mixtures of amphiphilic compounds that included fatty acids, fatty alcohols, polycyclic aromatic derivatives, and perhaps even fatty acid esters with glycerol. It stands to reason that such mixtures are much more probable than pure compounds given the complexity of the prebiotic environment. We have begun to investigate binary mixtures and have discovered that the addition of a fatty alcohol to fatty acid membranes dramatically increases their robustness to pH effects. For example, pure fatty acid vesicles become micelles only above pH 7.5; however, addition of 20 mole percent of the equivalent-chain-length fatty alcohol results in vesicle formation from pH 7 to pH 11 (Apel et al. 2002). We have also discovered that a simple glycerol ester of a fatty acid (glycerolmonodecanoate) readily formed stable membranes at pH ranges and divalent ion concentrations that were prohibitive for the pure fatty acid system (Monnard et al. 2002).

Proposed Research. The preliminary results above reveal that a rich chemical phase space remains to be explored in the search for amphiphilic components that would form stable vesicles under plausible prebiotic conditions.

Co-Is Deamer and Hazen propose to explore vesicle formation systematically in mixed-amphiphile suites. Our previous studies of vesicle formation in pure water have relied on either pure lipid species, such as long-chain carboxylic acids and alcohols, or on chloroform-soluble extracts from natural or synthetic samples. We propose to extend these studies to more diverse mixed suites of amphiphiles, as well as to aqueous solutions that include realistic concentrations of ionic species. We will start with a mixture of decanoic acid, decanol, glycerol monodecanoate, and hydroxypyrene, all of which are expected to be present in meteoritic organic components, or to be products of simulated geochemical syntheses. Aliphatic chain length will be chosen to be sufficiently long for stability, yet still fluid at ordinary temperature ranges. The head groups (-COOH, -OH, glycerol ester) are chosen for their ability to provide hydrophilicity as well as stabilizing effects of intermolecular hydrogen-bonding. Hydroxypyrene is chosen as a cholesterol analog, to serve as a stabilizing component of contemporary membranes through van der Waals interactions with non-polar lipid chains. The concentrations of components will be systematically varied over molar ratios ranging from 0 to 4, and the resulting structures will be analyzed microscopically. Analysis of membrane function will include measurement of permeability coefficients of the resulting membranes to amino acids (Chakrabarti & Deamer 1994), solute ions such as protons and potassium (Paula et al. 1996), and substrates such as nucleotides (Monnard & Deamer 2001). We will also establish the ability of the resulting vesicles to encapsulate macromolecules such as RNA and polymerase enzymes (Shew & Deamer 1983; Chakrabarti et al. 1994).

A second research focus involves the study of vesicle formation in model marine environments. We propose to examine suites of amphiphilic molecules described above as models for vesicle formation in plausible marine environments. As the concentrations of ionic solutes and the pH of early Earth sea water is still uncertain, we will vary the primary ionic species over plausible ranges in order to determine the extent to which a given amphiphilic mixture can form stable membrane structures. For example, NaCl will be varied from 0 to 1.0 M, divalent cations such as magnesium, calcium, and iron will be varied from 0 to 20 mM, and pH will be varied from 5 to 9. We expect that the results of these experiments will help to constrain the range of prebiotic aqueous environments and amphiphilic molecular species that could have promoted vesicle formation on the prebiotic Earth. A modern phospholipid, such as phosphatidylcholine, is able to form stable lipid bilayers over the entire range of environmental conditions described above. If we can discover a mixture of plausible prebiotic amphiphiles that matches this property in terms of stability and permeability, this result would provide an important stepping stone toward a better understanding of the origin of cellular life.

5.5.2 Molecular selection and organization on mineral surfaces (Astrobiology Roadmap Objective 3.2)

Background. Life's origin must have been preceded by the selection and concentration of monomers into macromolecules. Mineral surfaces are particularly interesting in this regard as it is well known that minerals provide sites for adsorption of key molecules in an aqueous environment (Bernal 1951). The potential effectiveness of crystalline surfaces in concentrating and organizing pure organic molecules has been demonstrated dramatically by the work of Sowerby et al. (1996, 1998a), who examined the adsorption of monolayers of the nucleic acid bases adenine and guanine on graphite and molybdenum disulfide surfaces. Such adsorption of pure molecules from solution results in highly ordered, two-dimensional organic structures, which might serve as templates for further organic selection and organization (Uchihashi et al. 1999).

Crystalline surfaces also may promote the emergence of one-dimensional molecular structures, in particular on surfaces that were subject to cycles of wetting and drying (Orgel 1998). Pioneering studies by Lahav and coworkers demonstrated peptide formation on clays subjected to cycles of wetting and evaporation (Lahav et al. 1978). Ferris and coworkers (Ferris et al. 1996; Ertem & Ferris 1996, 1997) and Orgel and coworkers (Hill et al. 1998; Liu & Orgel 1998) have demonstrated the oligimerization of amino acids on illite and hydroxyapatite and of nucleotides on montmorillonite. Other researchers have proposed similar roles for zeolites (Smith et al. 1998, 1999), hydroxides (Arrhenius et al. 1993), and calcite (Hazen et al. 2000), as well as for transition-metal sulfides, e.g., pyrite and pyrrhotite (Wächtershäuser 1988, 1992; Russell et al. 1993; Russell & Hall 1997; Brandes et al. 2000). Note, however, that all experiments on organic adsorption by minerals have been performed with relatively concentrated, pure solutions of the target organic species, rather than with a more realistic dilute and complex solution appropriate to the primordial Earth.

Hazen and Sholl (2002) have recently provided evidence that silica surfaces, quartz $(10\bar{1}1)$ and (001) faces, have the ability to select basic amino acids from a suite of acidic and neutral amino acids. This behavior is attributed to the difference between the point of zero charge of the mineral surface (pH ~ 3.5) compared with the amino acid isoelectric point.

The demonstrated ability of minerals to select and adsorb organic molecules has long been recognized as a possible mechanism for one of life's most distinctive biochemical signatures – its strong selectivity for L-amino acids and D-sugars. Almost all prebiotic synthesis reactions yield essentially equal amounts of L- and D-enantiomers (Lahav 1999; Mason 2000). Thus, to explain life's chiral excess two broad categories of symmetry-breaking phenomena have been invoked (Pályi et al. 1999; Bonner 1991, 1992, 1995). On the one hand, some researchers favor large-scale processes such as chirally selective photolysis by circularly polarized synchrotron radiation from a rapidly rotating neutron star (Clark 1999; Podlech 1999; Bailey et al. 1998), magnetochiral photochemistry (Rikken & Raupach 2000), or parity-violating weak interactions of nuclear particles (Salam 1991). It is possible that any of these processes may account for the small but significant excess of L-amino acids reported from some carbonaceous chondrite meteorites (Engel & Macko 1997; Cronin & Pizzarello 1997; Pizzarello & Cronin 2000).

On the other hand, many investigators have focused on chiral enhancement via local "asymmetric agents" (Popa 1997; Avetisov et al. 1991; Avetisov 1999; Cintas 2002). Some mechanisms rely on local amplification of slight chiral excesses, for example by Bose-Einstein condensation (Chela-Flores 1994) or by chiral self-assembly of polymers (Bolli et al. 1997; Lippmann & Dix 1999; Saghatelian et al. 2001) or crystals (Eckert et al. 1993; Lahav & Leiserowitz 1999). These and other chiral selection mechanisms (Bonner 1991) require further investigation, but the conceptually simple and geochemically relevant chiral selection mechanism of adsorption on chiral crystal growth surfaces of minerals, described above, has been largely overlooked.

Some authors argue that quartz and other minerals cannot contribute to the origin of biochemical homochirality (Bonner 1995) because left- and right-handed surfaces are present on Earth in equal abundance (Frondel 1978; Evgenii & Wolfram 2000). This argument is based on the assumption that the preponderance of L-amino acids in biology is evidence for a global prebiotic excess of L-amino acids rather than a chance selection in a local chiral environment. Nevertheless, both global- and local-scale chiral processes are deserving of further study.

Research to Date. Selective adsorption of a chiral molecule on a crystalline surface implies at least three non-colinear points of interaction between the molecule and an acentric solid surface (Davankov 1997). Consequently, chiral adsorption requires both a chiral molecule and a chiral crystalline surface (Hazen & Sholl 2003). The properties of chiral molecules have been studied for more than a century and a half (Pasteur 1848, 1851), and chiral chemistry is a thriving branch of organic chemistry (Stinson 2001; Rouhi 2002). The subject of chiral crystalline surfaces, however, has received relatively little attention, and many previous studies of chiral adsorption have failed to exploit these surfaces effectively.

Crystals that lack a center of symmetry provide the most obvious chiral surfaces for experimental study. Quartz (SiO_2; trigonal space group $P3_221$ or $P3_121$) is by far the most common acentric mineral in nature, and almost all experimental studies of chiral adsorption have thus focused on the symmetry-breaking effects of right- versus left-handed quartz (Tsuchida et al. 1935; Karagounis & Coumonlos 1938; Bonner et al. 1974, 1975; Soai et al. 1999). However, all of these studies employed quartz crystals that were powdered, a procedure that averages potentially strong adsorption effects on different faces, while destroying all structural information that might reveal adsorption mechanisms. Consequently, we have developed techniques to study adsorption on relatively large surfaces (~10 cm^2) of single crystals.

Centric crystals also provide a rich variety of chiral solid surfaces for study (Lahav 1999; McFadden et al. 1996; Hazen et al. 2001), because any crystal plane with a surface structure lacking mirror symmetry is intrinsically chiral. Most common rock-forming minerals display crystal growth faces that meet these conditions (Dana 1949; Smyth & Bish 1988). We have concentrated on the common and biologically relevant mineral calcite ($CaCO_3$; rhombohedral space group $R\bar{3}c$; Hazen et al. 2001). As a test of chiral selective adsorption, Hazen et al. (2001) immersed four calcite crystals for 24 hours in a 0.05-M solution of racemic aspartic acid. Enantiomeric faces equivalent to $(21\bar{3}1)$ and $(3\bar{1}\bar{2}1)$ displayed up to 10% preferential adsorption of D- and L-aspartic acid, respectively. By contrast, no selective adsorption was observed on rhombohedral $(10\bar{1}4)$ cleavage faces, which have centric surface structures and thus serve as an experimental control. This study of the calcite-aspartic acid system is the first experimental demonstration of significant chiral selectivity by a centric natural crystal.

Proposed Research. A focused program of study of molecular selection on calcite and quartz surfaces is now supported by a grant to Co-I Hazen from NSF. However, numerous promising aspects of the problem remain unstudied. With the support for an NAI Fellow, Co-I Hazen proposes to expand significantly on these developments with three complementary series of experiments: (1) differential adsorption of biomolecules, (2) origins of biochemical homochirality, and (3) condensation polymerization of homochiral peptides.

We plan to continue our studies of the relative adsorption of different amino acids, sugars, and other molecular species onto mineral surfaces, including new investigations of transition-metal oxide and sulfide minerals, exposed to equimolar suites of molecular species in aqueous solution. The objective is to determine the extent to which minerals might have selected and concentrated useful monomers from a complex prebiotic “soup.” Such selective molecular adsorption on sulfide surfaces is an important yet untested mechanism in the origin models of Wächtershäuser (1988, 1992), Russell & Hall (1997), and Russell et al. (1993, 1998). This effort, which will employ the experimental and analytical procedures developed by Hazen et al. (2001), will tie in closely to our studies of sulfide mineral-mediated organic reactions (see **Section 5.4.2**).

We plan as well to expand our measurements of the relative adsorption of enantiomeric molecular species, including amino acids and sugars, onto prepared chiral surfaces of pyrite and magnetite. Pyrite and magnetite are centric minerals, but any arbitrary cut section is likely to offer a chiral surface structure for study (Hazen & Sholl 2003). Accordingly, we will prepare a variety of surfaces (> 5 cm^2) from natural single crystals. This effort will require modification of existing techniques to anneal and characterize specific crystallographic surfaces. We will expose these surfaces to equimolar mixtures of racemic amino acids and pentose sugars. For example, in one series of experiments we will employ six amino acids (GLU+D, L-ALA + D, L-GLU + D, L-ASP + D, L-TYR + D, L-LYS) that are easily resolved by GC techniques. After 24 hours of immersion, the surfaces will be washed in water and the absorbed amino acids will be recovered via HCl washing (Hazen et al. 2001). These experiments will then reveal the relative adsorption of different amino acids as well as chiral adsorption.

Finally, we plan to initiate new studies of polypeptide formation on calcite crystal surfaces, which have a demonstrated ability for chiral selection of amino acids (Hazen et al. 2001). In our initial effort, we will adsorb aspartic acid onto a $(21\bar{3}1)$ terraced growth surface of a scalenohedral calcite crystal. Hazen et al. (2001) interpreted the enhanced adsorption of aspartic acid to be the result of preferential adsorption along the step regions of terraced surfaces. We will apply N-ethyl-N'-dimethylaminopropyl-carbodiimide (EDAC) as a condensation polymerization agent (Ferris et al. 1996; Liu & Orgel 1998) to such a prepared surface and desorb the resultant oligomers. Desorbed amino acid oligomers will be analyzed intact with a Surface Enhanced Desorption Ionization Time-of-Flight (SELDI-ToF) mass spectrometer in collaboration with Co-I Fogel and High-Performance Liquid Chromatography (HPLC) with Co-Is Scott and Tuross. Once we have established that we can oligomerize amino acids, we will establish the extent to which the oligopeptides exhibit chiral excesses using chiral selective columns with either GC-MS (in the case of short oligomers) or HPLC.

5.6 Life in Extreme Environments

Does the adaptability of life in extreme environments on Earth yield clues to the potential for life existing elsewhere in the Solar System? Over the past quarter century there have been tremendous advances in our understanding of the versatility and adaptability of life on Earth. Life clearly exists at extremes of both heat and cold, at low and high pressures, and under extremes of chemical environment (e.g., acidic and hypersaline). Precisely establishing environmental boundaries to microbial viability has become harder. With this increased uncertainty comes the slightly increased probability of discovering life, or the vestiges of life, elsewhere in the Solar System. As part of its contribution to NAI, the CIW team will explore life under extremes of habitat and under extremes of adaptive response.

5.6.1 Life in deep-sea hydrothermal vents (Astrobiology Roadmap Objective 5.3)

Background. A general focus of the CIW NAI team is to understand better the earliest stages in organic chemical evolution from chiral selection of organic precursors to non-enzymatic catalytic systems for generating metabolic reactions and pathways (see **Sections 5.4.2** and **5.5**). Much of this work was derived and has evolved from theories that linked the properties inherent to submarine hydrothermal vent environments and the microbial communities they support. Recently, it has been shown that minerals can provide certain critical functions, both by selectively absorbing organic compounds (Hazen et al. 2001) and by providing catalytic surfaces for synthesis of organic compounds (Heinen & Lauer, 1996; Huber & Wachtershäuser, 1997; Cody et al. 2000, 2001, 2003b,c). These results help constrain models for the earliest stages in the evolution of metabolic pathways and the transition from inorganic-mediated catalytic reactions to protein-enzyme driven systems. These results also lead to the hypothesis that early microbial communities may have relied on minerals to provide nutrients for survival.

Research to Date. During the past five years of the CIW-NAI project, Co-I Baross and his students at the University of Washington have obtained considerable information regarding the microbiota that survive and thrive in the vent chimney walls at deep-sea spreading centers. Specifically, we have obtained evidence of an intimate link between minerals and microbial viability through microscopic and molecular phylogenetic analyses of microbial communities in hydrothermal vent environments, as well as detailed physiological characterization of the vent microorganisms (Figure 5.6.1). Our microscopic and molecular analyses of active sulfide chimneys reveal that microbes exist throughout the chimney structure and are found even in zones that have experienced temperatures considerably greater than 100°C based on mineral compositional constraints (Schrenk et al. 2003). Two observations from this study were particularly surprising. First, there are microbial communities, detected optically with DNA-specific fluorescent stains and RNA probes, which inhabit the hot interior zones of the sulfide chimney. All of the organisms belong to the Archaea and most could be detected with RNA probes indicating that they may be viable and active. Secondly, in all cases the microbial communities exist as biofilms. The prevalence of biofilms consisting of archaeal communities on minerals under the extreme conditions found in sulfide chimneys suggests several interesting hypotheses that we propose to test. These are:

1. Thermophilic and hyperthermophilic heterotrophic archaea from vent environments grow on carbon either absorbed on mineral surfaces or on organic material synthesized on mineral surfaces.

2. These microbes derive key inorganic nutrients, such as the electron acceptors Fe (III) and Mn (IV), phosphorus, and other essential minerals, from insoluble minerals, e.g., apatite.

3. Some non-enzymatic catalytic reactions mediated by hydrothermal vent chemistry may substitute for enzymatic catalytic reactions in some thermophilic and hyperthermophilic archaea.

4. The microorganisms associated with biofilms on minerals show enhanced survival under extreme conditions of elevated temperature and pressure, desiccation, high salt, and high levels of radiation.

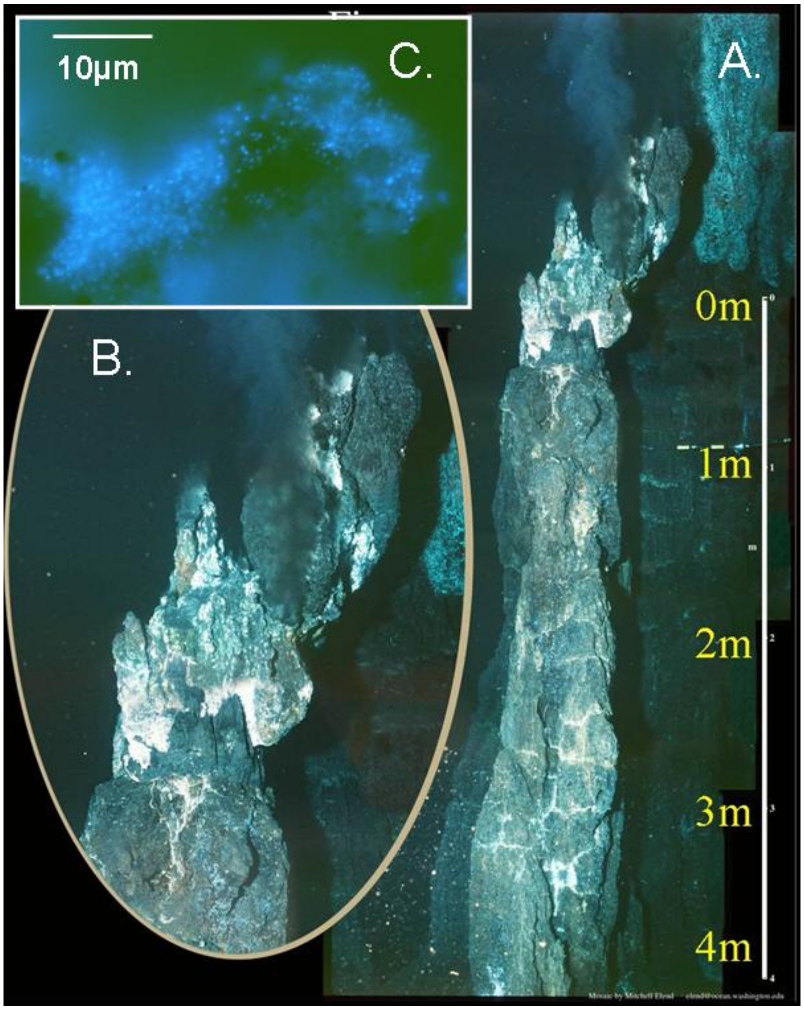

Figure 5.6.1. The black smoker sulfide chimney Finn (A) was recovered from the Mothra Vent Field on the Endeavour Segment of the Juan de Fuca Ridge in July 1998. Finn was venting 302°C fluid upon recovery (B, close-up of Finn) and contained complex mineralogical gradients within its walls. The structure was sampled by Co-I Baross for co-registered microbiological and petrological studies. Attached microbial communities, some of which formed 10-μm-thick biofilms (C), were observed, by use of fluorescent probes, throughout the structure, including high-temperature regions near the central vent conduit.

Proposed Research - Testing Hypotheses 1 and 2. Organic compounds can be abiotically synthesized utilizing a variety of energy sources, including heat, ultraviolet light, electrical discharges, meteor impacts, and radionuclide decay. Some of the compounds produced include hydrocarbons, amino acids, organic acids, and insoluble polymers of unknown composition. Recently, both acetate (Huber & Wächtershäuser 1997) and pyruvate (Cody et al. 2000) were synthesized abiotically in the presence of metal sulfur compounds under conditions that coarsely mimic those at hydrothermal vents. We have isolated a group of hyperthermophilic archaea from both crustal and deep hot sediment environments that can grow anaerobically on acetate using Fe (III) as the electron acceptor. Based on 16S rRNA sequence analysis, these subseafloor isolates are new genera within the Family *Thermococcales*, and they are also the deepest-rooted organisms within this group (Summit & Baross, 1998). They appear to be using acetate and Fe (III) in classic dissimilatory iron-reduction fashion (Lovley & Phillips, 1988). Unlike many organisms that can reduce soluble iron-organic compounds, these isolates reduce Fe (III) from insoluble minerals. They accomplish this by first attaching to the minerals where they generate organic polymers and biofilm. Recently, a new genus within the *Geobacteraceae* was isolated from a hydrothermal vent environment (Kashefi et al. 2003). Unlike other members of the *Geobacteraceae* that are mesophilic and can use a very limited number of carbon sources, this new isolate is thermophilic and can grow anaerobically on a wide range of organic compounds. These organisms would be excellent candidates for testing hypotheses 1 and 2.

We propose to test these isolates for their ability to oxidize carbon sources commonly synthesized abiotically using Fe (III) as the electron acceptor. In this regard, this proposed research complements some of the work outlined in **Section 5.4.2**. The carbon sources will include low-molecular-weight acids, hydrocarbons, ketones, and other compounds shown to be synthesized abiotically (e.g., Heinen & Lauwer 1996; Huber & Wächtershäuser 1997; Cody et al. 2000, 2001, 2003b,c).

We will also continue our efforts to isolate new hyperthermophilic microorganisms that use other transition metals as electron acceptors and determine the mineral products formed from microbial reduction. Such mineral phases may constitute important biosignatures for detecting life (see **Section 5.7**). Emphasis will be on isolating organisms that obtain all of their nutrients from organic material synthesized on mineral surfaces (see **Section 5.4.2**). One of our isolates uses acetate and Fe (III), attaches to insoluble iron oxides, and precipitates magnetite. Acetate utilization will be followed, along with the production of magnetite. This organism is also motile when not forming biofilms on minerals.

Proposed Research - Testing Hypothesis 3. There are a number of enzyme reactions that can be replaced by inorganic chemical catalysis (see, for example, Cody et al. 2001, 2003b). It is intriguing to consider whether there are extant microorganisms that take advantage of these catalytic reactions. If there are, from a prebiotic point of view did these reactions precede the advent of protein-mediated catalysis? There is evidence that some of the most ancient enzymes found in microorganisms involve catalytic reactions that can be accomplished without protein enzymes (e.g., Huber & Wächtershäuser 1997; Brandes et al. 2000; Cody et al. 2003b). Some examples include carbonic anhydrase, formate dehydrogenase, hydrogenase, nitrogenase, and acetyl CoA synthetase. All of these enzymes involve a metal-sulfur core and are thought to be ancient (e.g., Pereto et al. 1999).

The fixation of molecular nitrogen is particularly important and thought to be one of the most ancient of enzymes (Fani et al. 2000). The enzyme is also not specific for reducing N_2 to ammonia but can reduce most triple-bonded compounds including acetylene and cyanide (Silver & Postgate 1973). We propose a study focusing on nitrogenase and the search for this enzyme within archaea that populate vent environments in which sources of nitrogen other than N_2 are either limited or absent.

The conversion of atmospheric nitrogen to ammonia is widespread in microorganisms. Nitrogen fixation (*nif*) genes have been sequenced and analyzed from a large number of microorganisms (Ohkuma et al. 1999; Zehr & Capone, 1996). The *nif* genes are highly conserved in both bacteria and archaea. One of the interpretations from these data is that nitrogen fixation is an ancient trait and may have been present in the common ancestor before the separation of bacteria from archaea (Fani et al. 2000). Very little is known about the nitrogen cycle at deep sea hydrothermal vents. Ammonia has not been detected in subsurface vent fluids except at sites where there is overlying or buried sediments (Lilley et al. 1993). The dominant source of nitrogen to the hot subseafloor biosphere is N_2; however, nothing is known about nitrogen fixation by hyperthermophiles at vents. We propose to use molecular methods to search for nitrogen fixing genes (*nif*) in both an existing culture collection of hyperthermophilic archaea and in archaeal communities from subseafloor environments and to identify the groups of organisms, if any, that are actively fixing nitrogen. We will compare the sequence of these archaeal *nif* genes with other sequences in the database and determine if they show ancient lineages.

5.6.2 Stress adaption on microorganisms and expansion of habitability (Astrobiology Roadmap Objective 5.3)

Background. An interesting question regarding habitability is the nature of adaption as a means of expanding habitability. Recently Co-I Scott and Collaborator Sharma have shown that organisms that are not “adapted” for survival at high pressures are able to survive pressures approaching 2.0 GPa (20,000 atm) (Sharma et al. 2002). (For reference, this pressure is encountered at 60 km depth in the Earth.) Our approach uses a modified hydrothermal diamond-anvil cell to provide a “windowed” high-pressure environment. We have been able to show that these prokaryotes are able to carry out biochemical reactions at pressures up to 1 GPa (Figure 5.6.2). While we have not yet shown that replication occurs at these elevated pressures (a focus of current work), we have shown that when the pressure is released back down to approximately 1 atm the cells remain viable and are able to replicate.

Proposed Research. Co-I Scott proposes to investigate the mechanism(s) that allow cells to adapt to pressures well above those usually encountered by microorganisms such as *Shewanella oneidensis* and *Escherichia coli.* Pressure provides a model system to study stress adaption. In the natural world, stress involved with increased pressure will likely be linked to thermal and chemo-osmotic stresses. Three sub-tasks will be pursued: (1) proteomics and genomics of stress adaptation, (2) subsurface microbiology, and (3) microbial interaction with hydrates.

In the first sub-task, Co-I Scott and Collaborator Sharma will apply molecular biological analysis coupled with further refinement of high-pressure experimental methodologies (in collaboration with Co-I Hemley) at CIW. We seek to identify specific proteins and genes that are involved in the adaptation of these two ubiquitous pressure-sensitive bacteria. In this regard we are well situated at CIW, because of the unusual mix of scientific expertise and instrumentation available. For example, in addition to state-of-the-art diamond-anvil cell technology available in the high-pressure laboratory, we have a SELDI-ToF mass spectrometer obtained by Co-I Fogel with partial financial support from the NAI. This instrument is well suited to allow us to build fatty acid and protein profiles for organisms that have grown under extreme conditions (e.g., elevated pressures). Such profiles then can be compared with those of the organisms grown at ambient pressures, which will enable us to target specific classes of proteins that signature stress adaptation. Analysis of the lipid fractions will allow us to follow changes in membrane composition. We also have a DNA chip maker and reader (in collaboration with Co-I Steele) that will allow us to exploit the copious genome data that reside in public gene databases (e.g., TIGR and/or GeneBank).

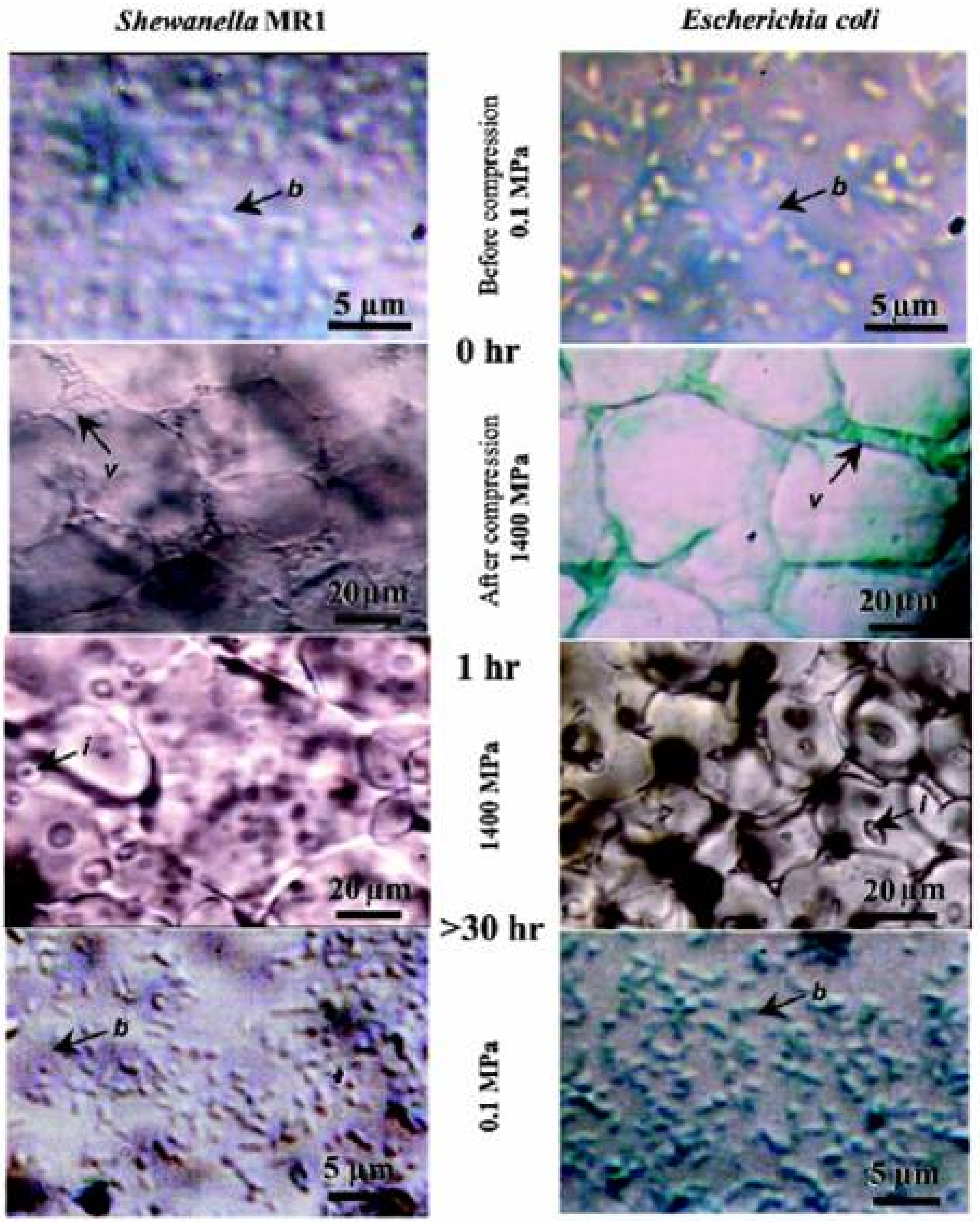

Figure 5.6.2. Microbial activity and viability in ice-VI (1400 MPa). Upon ice nucleation (0 hr, 1400 MPa), organic fluid veins (v) filled with bacteria (*Shewanella* MR1 on the left, *E. coli* stained with methylene blue on the right) appear. After ~ 1 hr, textural changes occur in the ice, defined by the formation of organic-rich inclusions (i) containing motile bacteria. Viable and countable bacteria were observed upon subsequent lowering of pressure (Sharma et al. 2001).

In concert with the proteomics work, genome analysis will provide us with an overview of how the organisms turn on genetic regulons in response to pressure. It will also provide clues to how the cells sense when pressures elevate to stressful levels. We plan to establish a genetic database and tools to ascertain whether the response in *Shewanella* and *E. coli* are unique or are ubiquitous in prokaryotes, without having to repeat the procedures carried out in the hydrothermal diamond anvil cell with hundreds or thousands of bacteria. The answer to that question bears on whether the response to elevated pressures is tied to a general stress response to the environment and whether all life on Earth still has the history of these survival mechanisms encoded within their genes.

It has become clear that a large portion of the biomass of the planet is located in the subsurface. Current estimates vary from 30% to 70%. Very little is known, however, about the geochemistry and biology of these ecosystems. There are a number of deep drilling programs being launched in the U.S., Japan, and elsewhere. However, the cost benefits and sampling difficulties will make any progress in this area slow. We have considerable experience in high-pressure experiments. We will apply and refine our methods to test bacterial growth models. These efforts will be directed at determining the best means for isolation of organisms from the subsurface. We are particularly well situated for working with samples from deep drilling expeditions to isolate subsurface microbes. The deep subsurface, sheltered from global events that have episodically altered the evolution of life on the surface and in the oceans, may provide the best environment for finding the closest extant relatives to a common ancestor. For this reason our NAI research into laboratory simulations of extreme environments will benefit from the collaborative field component with Co-I Baross (see **Section 5.6.1**). Combined, these efforts will provide valuable guidance to fundamental questions on the evolution of life and benefit the design of experiments aimed to search for life on Mars and, perhaps later, Europa.

Enormous stores of gas hydrates are located on the deep continental shelves of our planet. How these hydrates were formed and whether they constitute a viable environment for microbial communities remains uncertain. Our ability to create in the laboratory methane, CO_2, and other geochemically-relevant hydrates under realistic conditions will allow us to determine, *in situ*, whether microbes or microbial consortia can utilize such hydrates to support essential life processes. Toward this end Co-Is Scott and Hemley and Collaborator Sharma propose to study how pure microbial cultures as well as microbial consortia are able to interact with hydrates and elucidate metabolic mechanisms by obtaining kinetic data via microscopic and spectroscopic probing (for example, we can apply micro Raman spectroscopy to follow the loss or gain of a given substrate accompanying metabolism, as was used by Sharma et al. 2001).

Further, we will investigate whether microorganisms influence the generation of methane hydrates, as there is still a great deal of debate regarding whether natural hydrates might have biological origins (Paull et al. 1994; Brooks et al. 1994). Our work on hydrates has implications for examining the geochemistry of the outer planets, because much of the volatile inventory in the outer planets may be in the form of hydrates. Hydrates could thus be an important source of energy and carbon for non-Earth ecosystems. Hydrates may also sequester organic-rich fluids that might provide a low-temperature aqueous environment for life in the subsurfaces of cold “icy” environments, such as Europa and the polar caps on Mars.

5.6.3 Iron-based metabolic strategies for microbial life (Astrobiology Roadmap Objective 5.1)

Background. Iron is the fourth most abundant element in the Earth’s crust and one of the most abundant redox elements in the Solar System. Oxidation and reduction reactions involving this element provide energy for the growth of some groups of microorganisms, and it is postulated that Fe-metabolism is among the most ancient forms of microbial metabolism. Among microbes that obtain fuel from the oxidation or reduction of Fe, circumneutral Fe-oxidizing bacteria (FeOB) are the least understood. For many years, pure cultures of this group of bacteria were not available, and basic physiological studies were thus not possible. Now that a number of freshwater and marine isolates are available, crucial questions regarding carbon and nitrogen metabolism can be answered (Emerson and Moyer 1997).

Proposed Research. In the context of this proposal Co-Is Emerson, Fogel, Hauri, and Scott, and Collaborator Kehm propose to apply C and Fe isotopic methods to investigate several fundamental questions about this group of organisms. We will investigate autotrophy using ^{13}C tracer studies, and we will track the fractionation of stable isotopes in the metabolic intermediates as a consequence of anabolic synthesis. We will study Fe-isotope systematics to pursue some intriguing preliminary findings that FeOB are capable of causing a detectable mass fractionation of Fe isotopes and assess whether such organisms impart a robust biosignature (see **Section 5.7**).

Our initial studies will be directed toward providing evidence that our model pure culture organism, *Siderooxidans lithotrophicum* ES-1, is an autotroph. We propose to grow gradient tube cultures of ES-1 with $NaHCO_3$ that is enriched in ^{13}C (2.1 atom %). Although the carbon source could be enriched in ^{13}C by as much as 99 atom %, new cellular material will be readily apparent above the natural abundance level of ^{13}C (1.1 atom %) using isotope ratio monitoring mass spectrometery (IRMS). In order to concentrate the cells, the iron oxides must be removed by a low-speed centrifugation followed by centrifugation of the supernatant. The $^{13}C/^{12}C$ composition of the cellular material will be analyzed by standard mass spectrometric stable isotopic techniques in collaboration with Co-I Fogel. Preliminary calculations indicate that the yield of cells from a typical gradient tube culture will provide sufficient carbon necessary for high-precision stable isotopic analysis. Enrichments in ^{13}C of the ES-1 cells will provide confirmation of $NaH^{13}CO_3$ assimilation and autotrophic carbon fixation. In addition to ^{13}C, a parallel ^{14}C experiment will be conducted to confirm uptake of the radiolabel and a concomitant decrease in the dissolved inorganic carbon concentration.

In addition to this tracer approach, the isotopic fractionation factor during carbon fixation by ES-1 will be determined in laboratory experiments. The isotopic fractionation during carbon fixation by the Calvin cycle is approximately –20 ‰ (Madigan et al. 1989). The fractionation factor calculated in the study will provide further proof that the Calvin cycle is the carbon fixation mechanism for ES-1, or else it will point to the need to investigate other metabolic strategies. In addition, we will use the technique pioneered by Scott and Fogel (Scott et al. 2003) to analyze the fractionation of $\delta^{13}C$ in the individual amino acids (Figure 5.6.3) of these organisms to discern metabolic pathways for carbon incorporation.

Our preliminary studies of the iron isotopes in Fe-oxides collected from the Loihi hydrothermal vent site indicate that there is a significant fractionation toward heavier isotopes that may be indicative of a biological fractionation. Co-I Hauri and former NAI Postdoctoral Fellow Karl Kehm have developed new methods in iron isotope analysis using a multi-collector inductively coupled plasma mass spectrometer (ICP-MS) that are particularly well suited for these studies (Kehm et al. 2003). We have found that as bacterially precipitated oxides age, the degree of iron isotope fractionation approaches that of the surrounding basalt. We have observed that biogenically formed Fe-oxides are excellent substrates for the products of abiotic Fe-oxidation. These observations lead us to consider the following simple model to explain the evolution in iron isotopic fractionation recorded in iron oxides. First, we envision that microbes initially catalyze biological iron oxidation, precipitating oxides that record an isotopic shift of $\delta^{56}Fe \cong 0.5$ ‰; these oxides are precipitated in an organic matrix, and the initial ratio of biotic to abiotic FeOOH precipitation is > 1. As the FeOOH-organic matrix ages, the precipitation of additional Fe-oxides by purely chemical oxidation proceeds to drive the ratio of biotic to abiotic oxidation products toward zero and drives the bulk iron isotopic signature toward that of the surrounding basalt. If this phenomenon is general, it poses serious problems for the application of iron isotope systematics as potential biosignatures.

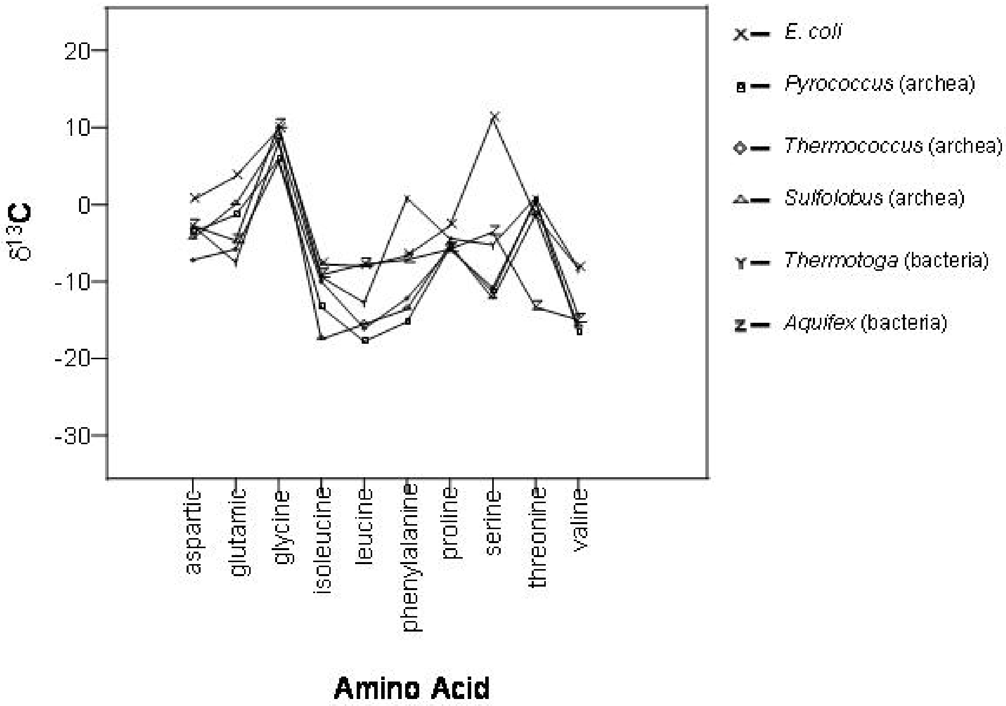

Figure 5.6.3. A graphical comparison of the stable isotopic composition of individual amino acids, normalized to the ^{13}C isotopic abundance of alanine, for a number of prokaryotes including *E. coli, Pyrococcus, Thermococcus, Sulfolobus, Thermotoga,* and *Aquifex*. The significant deviations in $\delta^{13}C$ clearly evident among many of the amino acids are indicative of differences in intermediary metabolism. These data, obtained as part of NAI-sponsored research of Co-Is Scott, Fogel, and Emerson, provide unique biosignatures of discrete metabolic pathways used by different prokaryotes.

We propose to explore this aging phenomena in a considerably different environment than that of the Loihi seamount, yet one where iron oxidation provides a key source of biologically useful energy. We will focus our studies on a local (to CIW and ATTC) field site that has Fe-rich ground water flowing through a small wetland. On the basis of preliminary observations, we recognize within this environment zones of very active growth of FeOB and other zones either at depth or on the edge of the flow regimen where the Fe-oxides appear much more aged. At this site, we will carry out a more complete iron isotopic survey to confirm and extend the results obtained from the Loihi seamount. In addition, we will perform aging experiments at the site by placing freshly collected oxidized material that has been poisoned with sodium azide to kill the microbes. These samples will be placed on site into mesh bags that have a pore size of < 0.2 μm that will exclude bacteria but will enable diffusion and flow of the Fe(II)-rich water, allowing continued abiotic oxidation to occur *in situ*. Parallel experiments will be conducted under more controlled conditions in the laboratory, where freshly collected material will also be subjected to different aging regimens in sterile laboratory media. We will apply multi-collector ICP-MS methodologies (e.g., Kehm et al. 2003) to use iron isotope fractionation to track the ratios of biotic to abiotic oxides. As a third component of these studies we will use pure cultures of lithotrophic FeOB isolated by Co-I Emerson to carry out similar aging experiments. Finally we will compare the isotopic signatures in Fe oxides formed by these lithotrophic organisms that oxidize Fe(II) as their energy source with heterotrophic Fe-oxidizers *L. discophora* and *S. natans* that grow using organic compounds as substrates yet precipitate Fe oxides biologically.

Finally Co-Is Emerson, Fogel, and Scott propose to continue their investigations into identifying metabolic pathways of extremophiles through isotopic analysis of individual amino acids (Figure 5.6.3). This work will involve specifically grown organisms both in pure culture and in mixed cultures to determine the efficacy of this method for use as a biosignature technique on mixed samples (see **Section 5.7**). Co-I Emerson will also continue to provide cultures and advice on S-isotopes using methods for analyzing the complete suite of S isotopes as pioneered by Co-I Rumble. In particular we will apply these molecular-isotopic approaches to our local field studies.

5.7 Biosignatures and Abiosignatures

What criteria reveal whether a suite of organic compounds are the result of microbial activities or non-biological processes? The difficulties associated with recognizing unambiguous biosignatures are underscored by recent scientific controversies over the quality of evidence for fossil life in Earth's earliest rocks (e.g., Schopf 1993; Mojzsis et al. 1996; Brasier et al. 2002; Fedo & Whitehouse 2002; Schopf et al. 2002; van Zuilen et al. 2002) and within the Martian meteorite, ALH84001 (e.g., McKay et al. 1996; Jull et al. 1998; Golden et al. 2000; Steele et al. 2000; Thomas-Keprta et al. 2001). The common denominator of these debates is the underlying difficulty of demonstrating conclusively the biogenicity of the respective evidence. A consensus has emerged from these discussions: Molecular evidence is critical, in addition to morphological evidence, to support extraordinary claims.

In this context, we argue that the convincing demonstration of an abiotic origin in any ancient terrestrial or Martian specimen with carbon-based molecules would also constitute an extraordinary finding, with possible implications for both the timing of life's origin and its subsequent radiation. Thus consideration should also be given to the search for abiosignatures – i.e., various chemical and physical characteristics that may point to likely abiological processes.

A principal difficulty in the search for unambiguous biosignatures and abiosignatures is that billions of years of diagenesis inevitably degrade physical structures and alter suites of organic molecules (whether biotic or abiotic) to assemblages of molecular fragments that rarely retain morphological information. Our challenge, therefore, is to identify diagnostic suites of ubiquitous and stable molecules and to develop analytical techniques for their reliable detection. We propose to tackle this objective by developing sensitive new analytical methods and applying these methods to relevant natural molecular suites from both biogenic and abiogenic processes.

5.7.1 Preservation of molecular biosignatures (Astrobiology Roadmap Objective 7.1)

Background. Organic geochemists have made considerable progress in the isolation, identification, and taxonomic attribution of biologically informative organic compounds in sediments. Several distinctive classes of molecules point unambiguously to the presence of life millions of years ago (e.g., Peters & Moldowan 1993). These compounds include pentacyclic triterpane hydrocarbons (so called hopanes), which are fossil remnants of biosynthesized hopanoids produced exclusively by bacteria as membrane components; sterane, which is derived from eukaryotic sterols; acyclic isoprenoids from various precursors, but particularly from lipids of archaea; and certain hydrocarbons derived from carotenoid precursors (Summons & Walter

1990). Other classes of compounds include porphyrin-based molecules from the diagenesis of chlorophyll and cytochromes and the associated isoprenoids. Apart from the porphyrins, these biomarker classes are collectively known as terpenoid hydrocarbon and are derived from isoprene monomer precursors. Hopanes, which are ubiquitous on Earth due to their resistant carbon skeleton (Innes et al. 1997), are generally regarded as unambiguous bacterial biomarkers (although a small number of eukaryotes also produce hopanoids, they are chemically distinct). Recent research reveals the presence of a specific cyanobacterial hopane (2-methyl hopane) in 2.7-Ga sediments (Brocks et al. 1999). This research shows that the diagenetic products of bacteria can be detected on Earth dating from a time near the end of the first half of Earth history, rendering this class of bacterial biosignature an interesting target molecule for planetary exploration.

The survivability of a biomolecule depends not only on its refractory properties, but also on the diagenetic environment and the burial conditions (e.g., pressure and temperature, pH, and redox potential). It appears likely that theoretically less refractory compounds such as squalene can be preserved up to at least 1.7 Ga (Summons & Walter 1990). Consequently, a main thrust of our research has been aimed at understanding the processes involved in the geochemical preservation of bacteria and methods to identify their fossil biochemical traces.

Proposed Research. In continuation of this research effort, Co-Is Steele, Tuross, and Vicenzi propose a program of analytical instrument development coupled with laboratory studies of fossilization, field studies, and analysis of relevant natural samples.

Co-I Steele and Collaborator Toporski propose to continue studies of morphological and biochemical characteristics of 25-Ma old bacterial biofilms from lacustrine sediments in Germany – an extension of previous work that led to the unambiguous identification of bacterial fossils (Toporski et al. 2002a). We have gathered a substantial amount of new sample material during the 2002 summer field season. We will further characterize the provenance of the organic substances contained in these samples, and we aim to establish chemical pathways by which biomolecules converst to fossil biosignatures. We will apply several analytical techniques, including Gas Chromatography-Mass Spectroscopy (GC-MS) and pyrolysis GC-MS in collaboration with Co-I Cody, HPLC with Co-I Scott, and *in situ* measurements using ToF-SIMS with Co-I Vicenzi, to identify comprehensively the organic inventory of the bacterial fossils. Surface Enhanced Laser Desorption Ionization-Time of Flight (SELDI-ToF) mass spectrometry and Protein Chip technology, in collaboration with Co-I Fogel, will be applied to test the samples for the possibility of protein/peptide preservation, as initial analyses have shown the presence of 6% N contained in the bacterial fossils.

Co-Is Steele, Tuross, and Vicenzi, working with Collaborator Toporski, propose to leverage the sub-micrometer localization of atomic and molecular ions offered by a Time of Flight-Secondary Ion Mass Spectrometer (ToF-SIMS) to help unravel chemical modifications that accompany the fossilization of simple organisms. This task will encompass two principal modes of operation: inorganic/organic molecular imaging (mass range is 1 – 10,000 AMU) on fresh fracture surfaces of known fossil specimens such as those from the Enspel Formation of Germany (Toporski et al. 2002a), followed by shallow 3D inorganic depth profiling of conventional thin sections.

The samples targeted for these investigations span ages from 14 million to 3.5 billion years and are in the possession of the investigators. These include laboratory fossilized bacteria and viruses; Enspel, Willershausen, and Messel oil shales (see Toporski 2002a,b); and Gunflint, Bitter Springs, and Apex cherts. Other techniques will be a valuable complement to ToF-SIMS and serve to provide ground truth for these investigations during both the imaging and chemical characterization of natural and experimental fossils. These include light microscopy with 3D rendering capabilities, high-resolution electron microscopy (FEG-SEM and TEM) (CIW, NRL), focused ion beam (FIB) (SI), scanning probe microscopy (CIW), and SELDI-ToF and GC-MS (CIW).

Co-I Tuross will use modern stromatolites as a model for long-term degradation of biochemicals and will focus on the types of cross links formed in extractable organic matter using multiple chaotropic agents. Chaotropic agents are compounds that disrupt the hydrogen bonding structure of water and enhance the solubility of non-polar organic compounds. The bioavailability of the organic matter in the stromatolites will be determined in a range of sequential enzymatic digestions, and the quantitative systematics of the cross-links in both enzymatically accessible and refractory material will be determined. Both reducible and nonreducible cross-links will be characterized and quantified using chemical, enzymatic and chromatographic (primarily LC) methods.

The characterizations of organic matter obtained via rigorous extraction with chaotropic agents will be compared with pyrolysate patterns (GC-MS) in order to assess the production of compounds in high-temperature conditions. Finally, a third preparation that involves removal of the mineral surround under the most gentle chemical conditions possible will be compared with pyrolysate and chaotropic extractions.

Co-I Steele proposes to amplify these studies through molecular characterization using a Protein Chip reader. Specifically, he will test whether the complex higher molecular weight compounds found in living organisms can be preserved and identified in the fossil record.

5.7.2 Studies of organic compounds and silicified microbial remains associated with the Kamchatka geothermal region (Astrobiology Roadmap Objective 7.1)

Background. There is considerable astrobiological interest in the geothermal hot springs of the Kamchatka Peninsula, situated in the far eastern portion of Russia. In September 2001, Co-I Deamer helped organize and attended an NAI-sponsored field expedition to Kamchatka (led by Sherry Cady, Portland State University), where Deamer and the other participants discovered the remarkable potential of this unique environment for research in astrobiology. The region spans a geographical area of approximately 400 by 1200 km and contains nearly ten percent of the world's active volcanoes as well as over 150 surface-exposed hydrothermal sites. The primary attraction of Kamchatka for the work proposed here is its isolation from potential sources of contaminants related to human activities. Furthermore, much of the volcanism occurs at high latitudes and altitudes, so that geothermal areas are available in which biological processes are entirely microbial. Numerous microbiologists (mostly Russians but including such Americans as Frank Robb of the University of Maryland, Jonathan Trent of NASA Ames, who also participated in the Kamchatka field expedition, Ken Stedmen of Portland State University, Juergen Wiegel of the University of Georgia, and many others) have investigated these hot springs in order to catalog the diversity of microorganisms present. It has recently been shown that some of the Kamchatka hot springs provide a home for an interesting group of anaerobic carbon-monoxide-oxidizing bacteria and archaea (Sokolava et al. 2002).

Astrobiologists find Kamchatka interesting not only for its intriguing microbial ecosystems but also because this locale may provide a modern example of the types of hydrothermal ecosystems that were active early in Earth's history. Similar environments were likely (and might still exist) at or near the surface of Mars. It is well known that rapid silicification provides an excellent means for the preservation of biomolecules, hence microbial biosignatures (e.g., Schultze-Lam et al. 1995; Cady & Farmer 1996; Toporski et al. 2002) (Figure 5.7.1). In the case of the Kamchatka, or Mars, any microbial communities trapped and encased in precipitating silica will likely retain a substantial amount of biochemical information for a considerable length of time. The unresolved question is whether the process of initial silicification is moderately or highly deleterious to biomacromolecules (Toporski et al 2002).

Co-I Deamer, in collaboration with Co-I Steele and Collaborator Toporski, propose to use the Kamchatka territory as a model environment to study possible geochemical synthesis of organic compounds and the extent of preservation of microbial biosignatures contained within mineral precipitates derived from the hot springs. It is well known that the numerous hydrothermal fields are highly variable in their fluid and volatile chemistry and can be divided roughly into five geochemical types with respect to the primary gases present: (1) H_2S - CO_2; (2) N_2 - CO_2; (3) CO_2; (4) N_2; (5) CH_4 and N_2 - CH_4. These differences in chemistry manifest differences in microbial biodiversity, as well as the types of minerals precipitated. Thus, the types of fossilized biosignatures preserved in each type of hydrothermal system will likely vary considerably, a circumstance that will allow us to explore the effects of natural variables such as precipitation chemistry and precipitation temperatures on the preservation of recognizable microbial biosignatures.

The Kamchatka region offers many pristine sites for astrobiological exploration. For example, Craternaya Bay on Jankicha Island, in the Kurile Archipelago and situated several hundred kilometers from Kamchatka, features unique hot-spring ecosystems that have been only cursorily explored (Tarosov et al. 1989). The bay, approximately 1.5 km in diameter and up to 60 m deep, is connected to the ocean by a narrow and shallow (less than 1-m deep) strait. Numerous hydrothermal vents are distributed from the floor of the bay all the way up to the surrounding mineralized shoreline of the bay. Other promising sampling sites include high-altitude geothermal springs on accessible volcanos such as Mt. Mutnovskiy, which is located approximately 40 km from Petropavlovsk. Even more accessible are numerous boreholes (associated with geothermal energy production) located near the city of Petropavlovsk and other settlements. These boreholes permit direct measurement of chemical and physical properties of deeper geothermal aquifers. For this proposed research we are particularly interested in samples of hydrothermal deposits that formed at known depths within the boreholes and that are available from drilling. A valuable component of the proposed research is the establishment of a collaborative relationship between the Russian Astrobiological Center and the CIW NAI team.

Proposed Research. The wealth of unique hydrothermal samples from Kamchatka provides the focus for a promising research program of sample collection and analysis. As a primary objective, Co-I Deamer proposes to organize a field expedition to Kamchatka during the summer of 2004 along the lines of the NASA-sponsored field trip he helped organize and participated in during the summer of 2001. Ideally, investigators from throughout the NAI as well as other interested parties would undertake further collaborative study of this extremely interesting environment. During this expedition, Co-I Deamer, in collaboration with Collaborator Toporski, would collect water samples for organic analysis and samples of silicified deposits at a variety of geothermal springs. Co-I Steele and Collaborator Toporski have been studying the preservation of microbial biomarkers and biosignatures by laboratory silicification (Toporski et al. 2002a). The collection and thorough analysis of natural silicified samples from the Kamchatka hot springs will therefore provide an excellent opportunity to test the predictions derived from their experiments.

The silicified samples will be returned to CIW where they will be analyzed using a number techniques, including quasi *in situ* TEM studies in collaboration with Co-I Stroud, pyrolysis-GC-MS and STXM (see below) with Co-I Cody, and an array of novel yet powerful bianalytical techniques, including antibody-based assays to specific cell components (e.g., lipo-polysaccharides, extracellular polysaccharides, purins, peptidoglycan), wherein fluorescent labels are used to report quantitatively on the concentration of a given target biomolecule. In order to observe and analyze intact proteins (if present) as well as detect any thermal breakdown products that may have accompanied silicification, Co-I Deamer will collaborate with Co-I Fogel to apply SELDI-ToF on demineralized samples (using the mild fluorination method derived by Fouad Tera (CIW) and outlined in Cody et al. 2002 and adopting the novel solubilization strategies derived by Co-I Tuross) to observe whether there are intact proteins or substantial protein fragments. These data will be correlated with the chemical characteristics of the hot springs from which the samples were obtained to see whether the preservation of biomolecular signatures of microorganisms is ubiquitous to silicification.

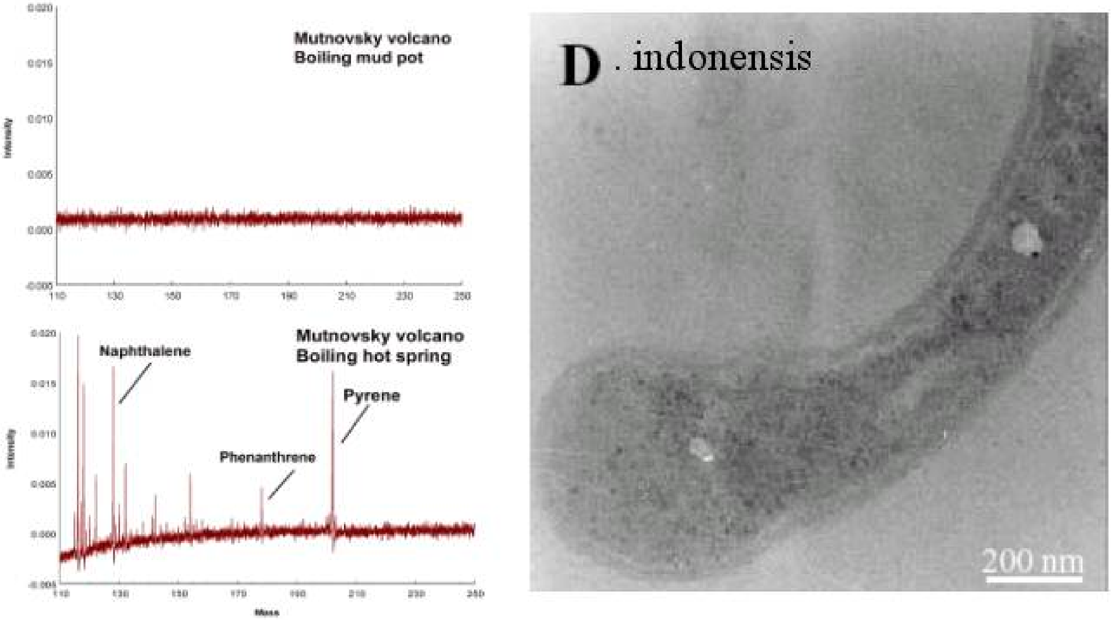

Figure 5.7.1. Left: laser desorption mass spectra of solute from Kamchatka hot spring waters. Note that only the spring contains organic compounds. Right: TEM micrograph of a cell of *D. indonensis* that had been exposed to mineralizing solutions of silica (1000 ppm Si concentration) for one week (Toporski et al. 2002). EDS spectra reveal considerable silicification around the cell membrane but minimal alteration of the cell structure. Experiments such as this will provide a basis for comparison with natural silicified samples retrieved from the proposed expedition to Kamchatka.

We further propose engage in research into the presence of DNA at the study site as well as in silicified materials. Co-I Steele and Collaborator Toporski would conduct field PCR (polymerase chain reaction) studies to allow the identification of target DNA, e.g., of archea and/or bacteria in the field. PCR products produced in the field can be returned to the laboratory for sequencing. The use of the field PCR reduces transportation issues, as original material does not have to be kept frozen after sampling until returned to the laboratory and further avoids sample contamination during transport and storage. Sequencing would help identify species present in the Kamchatka hot spring ecosystems. Silicified materials containing microfossils would be tested in the laboratory for the presence of DNA. Extraction of DNA from deposits of different ages and chemical environments would help us to understand the factors controlling DNA survivability in silicified deposits.

Co-I Deamer will collect water samples from each of the hot springs investigated. Total soluble carbon and nitrogen as well as bulk stable isotopic measurements will be assayed at CIW by combustion and mass spectrometry in collaboration with Co-I Fogel. Amino acid content and distribution will be determined in an amino acid analyzer. A freeze-dried aliquot of each sample will be derivatized by alkylation and reaction with trifluoroacetic anhydride in order to analyze for organic acids (including amino acids) via GC-MS. Co-Is Scott and Fogel will apply compound-specific isotope (nitrogen and carbon) ratio monitoring mass spectrometry to see whether these isotopic biosignatures can yield information on the prokaryotic sources and diversity based on their previous analysis of such isotopic signatures in a broad suite of prokaryotes (see **Section 5.6** for details and Figure 5.6.3 for example).

Finally, Co-I Deamer will explore whether free fatty acids and fatty alcohols are present in these hydrothermal systems. As discussed in **Section 5.5**, self-organizing, lipid-like compounds may have provided the mode of encapsulation for the first cells. Because it is unlikely that complex lipid biosynthesis pathways co-evolved with the first forms of life, it seems reasonable that the first cellular organisms used lipid-like molecules available in the environment. For example, suites of alcohols and monocarboxylic acids ranging up to 30 carbons in length have been produced under plausible prebiotic hydrothermal conditions by a Fischer-Tropsch reaction mechanism (McCollum et al. 1999). However, there have only been a few reports of unambiguous signatures of abiotic organic synthesis in nature (e.g., Sherwood Lollar et al. 2002). The paucity of reported abiotically synthesized organic carbon results, in part, from heterotrophic microbial activity. Heterotrophic microbes would rapidly remove all but the most recalcitrant abiotic organic species from most environments. Furthermore, there have been very few studies that have specifically sought to establish (or discriminate) between organic compounds synthesized abiotically from otherwise expected biological sources. The chemistry of the fluids from some of these hot springs is sufficiently reduced to support, at least theoretically, the abiotic synthesis of such lipids (e.g., Sokolava et al. 2002). Significantly, Isidorov et al. (1992) reported a series of organic compounds to be present in steam-gas outflows from Mutnovskiy. These included hydrocarbons up to 12 carbons in length. Remarkably, a variety of fluorinated and chlorinated hydrocarbons were also present, including difluorodichloro-methane, fluorotrichloromethane, chloroform, and tetrachloroethylene. The halogens are presumably derived from mineral sources deep in the volcanic rock matrix. If these observations are verified, then it is clear that some very interesting organic geochemical reactions are occurring in Kamchatka geothermal settings. For these reasons, Co-I Deamer, working in collaboration with Co-Is Fogel and Hazen, will seek to isolate such hydrocarbon derivatives and other soluble organic compounds from geothermal springs and use compound-specific isotopic analysis to ascertain whether the stable isotopic distributions can distinguish between abiotic synthesis and a biological origin of the organics.

5.7.3 Scanning transmission microscopy and *in situ* chemical analysis of organic fossils (Astrobiology Roadmap Objective 7.1)

Background. In **Section 5.3.1** we propose to apply scanning transmission X-ray spectro-microscopy (STXM) as a probe of extraterrestrial organic matter in meteorites with a focus on ultimately providing a robust means for analyzing extraterrestrial carbon, nitrogen, oxygen, and sulfur functional groups in IDPs and any organics contained within particles collected in the Stardust mission. STXM is also a very powerful tool to extract molecular biosignatures in ancient fossiliferous rocks.

It is well known that permineralization preserves plant and even microbial fossils in three-dimensional cellular detail (e.g., Boyce et al. 2001). The exquisite preservation of organic matter by silicification has long afforded opportunities for the study of anatomical evolution. Such preservation also raises the possibility that cell- and tissue-specific chemical analyses might also be possible, thus providing insights into biochemical and physiological evolution. The problem is that the amount of carbon preserved in permineralized fossils is generally very low (Boyce et al. 2001). Conventional, albeit powerful, analysis using either ^{13}C solid-state NMR or pyrolysis GC-MS require relatively large samples to be demineralized first to obtain sufficient material for these standard organic geochemical analyses (Collinson et al. 1998). While the quality of the chemical information from NMR or pyrolysis GC-MS is excellent, the demineralization unfortunately destroys the spatial-anatomical context of the organic matter that had been "locked" into place via silicification. When analyzing ancient fossils, this destruction becomes a serious problem as the majority of fossil organic matter has been altered substantially during diagenesis. In some cases this alteration is so severe that discrete molecular biosignatures no longer exist. This stated, there may still remain chemical differentiation at a very fine scale related to the initial presence of different biopolymers that can be used for biomolecular reconstruction.

Research to Date. In collaboration with Kevin Boyce and Andrew Knoll (Harvard-NAI; Boyce is a currently an NAI-NRC Fellow who divides his time between Harvard and CIW), Co-I Cody has recently developed methods that exploit the classic preparative techniques employed by paleontologists and paleobotanists coupled with a state-of-the-art X-ray synchrotron-based scanning transmission microscope (see **Section 5.3.1** for details). Recent advances in X-ray micro-focusing techniques coupled with brilliant, synchrotron-derived X-ray sources have led to the development of soft X-ray spectromicroscopy (Jacobsen & Kirz 1998) that allows for the analysis of functional group distributions in ancient bio-organic structures at spatial resolutions approaching 30 nm (Cody et al. 1995a,b, 1996, 2000; Boyce et al. 2002).

Recently Boyce and Cody applied STXM to analyze the signature of ancient biochemistry in 40- and 400-Ma fossils. Specifically, we applied carbon (1s) X-ray absorption near edge spectroscopy (C-XANES) to characterize the organic chemistry stored within structurally differentiated regions of tracheid cell walls in fossil plants (see Figure 5.7.2). For the purpose of comparison we included analysis of a modern extant tracheid cell wall from re d cedar *Juniperus virginianan*. Our selection of fossils included *Metasequoia milleri*, a conifer from the Middle Eocene (ca. 40 Ma) preserved in the Princeton Chert (Basinger 1981) and the stem lycopod *Asteroxylon mackiei* from the Early Devonian (ca. 400 Ma) preserved in the Rhynie Chert (Kidston & Lang 1920).

The power of soft X-ray microscopy is that we obtain image contrast through variations in carbon chemistry using a high-resolution monochromator (~ 0.03 eV) (Jacobsen et al. 1998)) tuned to the characteristic energy of specific core-level (1s) to bound-state (e.g., π^*) electronic transitions. Using this instrumentation, we have been able to observe chemically differentiated cell wall, even in the 400-million-year-old sample. Using C-XANES obtained from sub-micron analysis regions, the STXM reveals that carbon derived from both lignin and structural polysaccharides has been preserved within individual tracheids, albeit in a diagenetically transformed state (Boyce et al. 2002).

This result is remarkable for two reasons. First, this result constitutes an analytical "record" for the chemical detection of biomacromolecular differentiation within fossil cell walls. While individual molecular biomarkers have been detected in samples as old as 2.7 Ga (Brock et al. 1999), our observations reveal the oldest preserved chemical evidence of cellular differentiation, at 400 Ma. Second, and more importantly, detecting the presence of lignin in *Asteroxylon* may help explain the critical biomolecular evolutionary step that allowed early plants to colonize the continents.

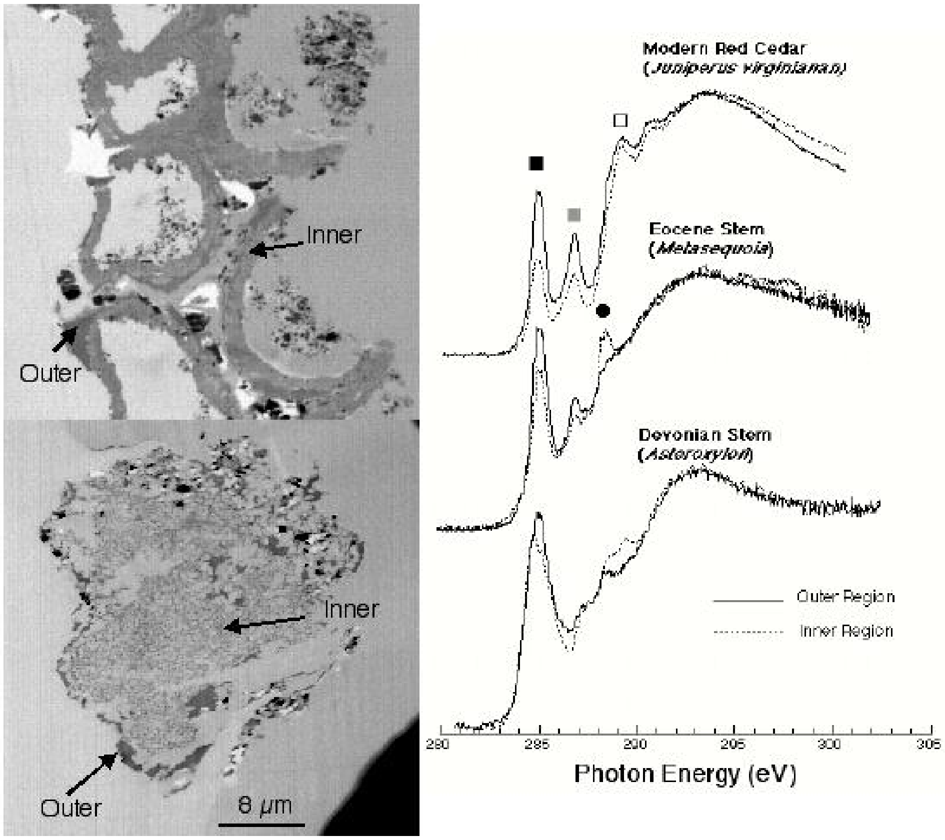

Figure 5.7.2. High-resolution STXM images (left) of preserved tracheid cells of ancient vascular plants, *Metasequoia milleri* (top), preserved in the ~ 40-Ma Princeton Chert and *Asteroxylon mackiei* (bottom), preserved in the ~ 400-Ma Rhynie Chert. These high-resolution (40-nm spot size) X-ray images (with the photon energy tuned to 286 eV) reveal a mechanically resistant, strongly absorbing outer region and a weakly absorbing inner region. Comparison of the C-XANES spectra from each region (shown on the right) clearly reveals significant differences in the carbon chemistry distinguishing the differentiated regions of the cell membrane even in the 400-Ma fossil (Boyce et al. 2002). The squares and circles highlight specific absorption bands corresponding to organic functional groups diagnostic of ligno-cellulosic and altered ligno-cellulosic material.

The global significance of such an evolutionary gain need not be expanded upon here. It is sufficient to note that the current global carbon, oxygen, and weathering cycles are strongly controlled by the presence of continental flora. The eventual rise of sentient vertebrates may well owe their existence to the first shallow marine plants that developed the ability to colonize the continents.

Proposed Research. The methods described in Boyce et al. (2002) are applicable to any sample, terrestrial or extraterrestrial, subject to the chemical constraints that the matrix material exhibits different solubility characteristics from the fossil carbonaceous material. As part of our commitment to the NAI as a whole, we offer our considerable experience in soft X-ray spectromicroscopy to any affiliate or external collaborator who has astrobiological science questions that would benefit from this unique analytical technology.

Co-I Cody plans to continue the development and refinement of methods for STXM analysis of ancient permineralized fossils. He will focus on analyzing microbial assemblages in the relatively young Enspel Formation with Co-I Steele and Collaborator Toporski. Co-I Cody will collaborate with Co-Is Deamer and Steele to apply STXM to analyze microbial material encased in silicified deposits collected from the expedition to Kamchatka. He will also focus on the analysis of organic fossils preserved in Proterozoic cherts from Western Australia with Co-I Rumble and Collaborator Ono. In each case the goal will be to derive molecular signatures from altered biomolecules, *in situ*, and provide more robust evidence for the existence of life in the early Earth's fossil record. One of the best means of assessing the provenance of organic matter is to analyze it *in situ* using technology such as STXM.

5.8 Astrobiotechnology (Astrobiology Roadmap Objective 7.1)

How can advances in biotechnology be used to further NASA's objectives to find and characterize life on other worlds? Over the last few years, enormous advances have been made in our understanding of the extent to which life can survive in apparently hostile and otherwise improbable environments. The significance of these revelations to NASA's Astrobiology Program lies in the fact that these observations increase the probability that life may exist elsewhere, e.g., Mars. The problem remains, however, that even if life does exist on certain extraterrestrial bodies, will we be able to detect it? Also, given the recent debate on the authenticity of the earliest fossil life on Earth (Brasier et al. 2002), it is important to utilize new techniques and philosophies to tackle these issues.

The principal driving force for the recent advances in molecular biology has been the advent of extraordinarily powerful and sensitive bioanalytical tools. The majority of these biotechnological developments have been fueled by medical considerations, and it is only recently (within the last decade and largely in response to NASA initiatives) that environmental microbiology (and the study of multi-species interactions) has risen as a viable scientific endeavor. There currently remain numerous poorly surveyed environments. For example, it is only recently that studies in Antarctica have begun to show the breadth and adaptation of life that exists there (Ward & Priscu 1997).

Clearly one of the limiting factors in microbial surveys has been accessibility to plausibly habitable environments. Surface and shallow subsurface environments, for example, are readily accessible; biological surveys of photoautotrophic microorganisms, e.g., cyanobacteria, are consequently comprehensive. On the other hand, studies of autotrophic, chemolithotrophic, and heterotrophic organisms, such as those that thrive at hot springs, at kilometer-plus depths in the oceans, or within deep crustal environments on the continents, remain unevenly investigated. From an astrobiological perspective, the development of strategies to investigate largely inaccessible (at least to manned scientific teams) environments on and within the Earth will lead to technology that benefits surveys on similarly inaccessible extraterrestrial environments, e.g., Mars.

The key to developing critical life-detection instrumentation for future NASA missions lies in the transfer of state-of-the-art biotechnology from medicine and biosciences to mission planning and its integration with other established techniques. However, the growth of biotechnology in the last 20 years has been staggering, and the sheer number of new techniques and procedures can be disorientating. The question arises as to which of the many methods currently available provide the greatest opportunities while at the same time achieve technical feasibility as spacecraft instrumentation packages. NASA's Astrobiology Program provides the natural interface between biotechnology and planetary science to address this question.

Why use biotechnology? The answer is simple; the techniques used for Solar System exploration have provided ambiguous conclusions or failed completely to detect life. In the case of the debate on relic biogenic activity in the Martian meteorite ALH84001, many traditional techniques such as amino acid analysis, C-isotope analysis, and gas chromatography - mass spectrometry (GC-MS) all yield the conclusion that no life was contained within the meteorite (McKay et al. 1996). However, some if not all of this entire meteorite has been colonized by terrestrial microbiota (Steele et al. 2000). A further example is the ambiguity associated with the Viking Lander results (Mancinelli 1998). Recent re-evaluations of these experiments have revealed that the sensitivity of the GC-MS was simply inadequate for the task and would have been unable to detect organic material produced by approximately 10^7 bacteria per gram of Martian regolith (Glavin et al. 2001). This same group points out that a newer instrument (Mars Organic Detector) is 100 times more sensitive than the Viking GC-MS, which presumably means that 10^5 bacteria/gram will remain undetected.

Current immunoassays, such as enzyme-linked immunosorbent assay (ELISA), are known to be 150 times more sensitive and a great deal more specific than the best laboratory-based GC-MS instruments (Li et al. 1999). For example, ELISA has been used in environmental waste water studies to detect specific estrogen hormones at levels as low as 0.05 ng/L (0.05 parts-per-trillion), and there is evidence to show that miniaturization of these instruments increases sensitivity (Huang et al. 1999). A wealth of microbiological, molecular, and genetic techniques is now being refined as biotechnology approaches its golden age. Nanotechnology has been integrated with biotechnology, resulting in exciting new fields of research with the development of robust "lab-on-a-chip" commercial instrumentation (see Auroux 2002 and Reyes et al. 2002 for extensive reviews). These include the Agilent bioanalyser 2100, Perkin Elmer's protein array workstation, the Biosite™ Triage system, and the Charles River Food Spoilage Detector, using Limulus Amebocyte Lysate (LAL) assay (which has single-cell detection sensitivity, Wainwright 1999). These instruments are extremely sensitive to target molecules, sufficiently robust to be used in hospitals and the food industry, and becoming tailored to environmental samples such as detection of agents of biological warfare.

In the case of the Agilent bioanalyser 2100, a range of microfluidic chips performs sample processing and capillary electrophoresis, and the resulting DNA/RNA/protein separation is detected using laser-induced fluorescence (www.agilent.com/lab-on-a-chip). Each of the other instruments contains a probe or probes (tagged with either an enzyme or fluorochrome) specific to a target. By simply changing the probe, one can make an instrument shift from detecting a food spoilage organism (using a probe to bacterial LPS) to detecting bacterial diagenetic products such as hopanes (using an anti-hopane antibody, recently developed and under testing at CIW and JSC, Maule et al. 2003). These techniques have already been developed to answer the same questions on Earth that we wish to address in the rest of the Solar System: is there or was there once microbial life present, what are its characteristics, how can we detect it in small quantities, and what effect is it having on the environment in which it resides (and vice versa). Whether it is a novel microbe in a black smoker, an unknown infection, or a cancer cell in the human body, the task, goals, methodology, and philosophy are the same. To the question, "Why use biotechnology for astrobiology to search for life?", the answer becomes, "Biotechnology was independently, and successfully, developed for the detection of trace levels of biomarkers on Earth, and need only be modified and applied to Solar System exploration" (Steele and Toporski 2003).

Originally designed for high throughput data mining of genomes, microarrays can fit up to several million separate tests per glass slide (Hoheisel 1997; Schena 2000). This technology is growing at an unprecedented rate and will revolutionize environmental microbiology (including issues relevant in astrobiology and geobiology). Although these tests comprise mostly DNA- and protein-based probes, their use can be diversified to tests using any reagents that produce a color change (either chromophore or fluorophore) during the detection of a primary molecule. The technology is commercially available and is being utilized to produce miniaturized, highly specific test kits for a range of organic compounds linked to life processes and indeed has been highlighted for further development by a number of agencies (Gibson 2002). These test kits could be tailored for use on all of the potential targets listed in Table 5.8.1. A further interesting possibility for the detection of extraterrestrial life arises if one considers integrating combinatorial chemistry with microarray technology. It would then be possible to produce millions of random probes per glass slide. For example, one could incorporate all the possible combinations of purine and pyrimidine bases that can combine into an information-storing system sufficiently complex to code for an organism. This vast coverage of plausible bases then reduces the assumptions needed for the detection of an extraterrestrial organism from DNA-based life to that of nucleic-acid-based life. These techniques may be further refined for use in experiments on the formation of life on Earth by screening large numbers of prebiotic reactions printed either onto glass slides or mineral interfaces.

It is essential to assess any biological-contamination background signal for organic analysis instruments to be used in any landed mission on another planet. Unambiguous detection and elimination of any terran contaminant signal is critical to show that any residual signal is indigenous to the Solar System body being explored.

In the case of astrobiological bioanalytical instrumentation packages for missions, it may be advantageous to “de-tune” specific bioanalytical instruments to the point that one obtains sensitive detection of discrete classes of biomarkers. This procedure would constitute a search strategy leading from a general terran signature to specific metabolisms, not only to identify life but potentially to define its nature. General classes of target materials of astrobiological interest are listed in Table 5.8.1.

Table 5.8.1. Classes of organic molecules of astrobiologic interest

Prebiotic/protobiotic molecules	Amino acids, purines and pyrimidines, polycyclic aromatic hydrocarbons, chain hydrocarbons, fatty acids, sugars and sugar derivatives, isoprenoids.
Terrestrial contaminating organisms	Whole cells, cell components (LPS, DNA, proteins, cytochromes).
Terrestrial contaminating organics	Condensation products derived from rocket exhaust, lubricants, plasticizers, atmospheric contaminants.
Terrestrial-like organisms	Transferred from Earth to an extraterrestrial body or have evolved on the extraterrestrial body in a manner similar to that by which life evolved on Earth. This conclusion could be reached only if procedural blanks had removed the possibility of hitchhiker contamination. Target molecules could include individual genes, membrane constituents, specific enzymes, and co-enzymes that would be expected to be over-expressed or adapted in ambient conditions.
Non-terrestrial-like organisms	Utilizes an array of molecules for information storage, information transfer, compartmentalization, and enzymatic activity that differ from those used by extant terrestrial life. An example would be the use of novel amino acids or nucleotides.
Fossil biomarkers	Detection of established terrestrial fossil biomarkers such as hopanes, archaeal lipids, and steranes, for the detection of the diagenetic remains of terrestrial-based life.

Proposed Research. Obviously the above discussion covers a greater scope than can be addressed by a single group. Co-Is Steele and Vicenzi propose the following tasks:

Co-I Steele will use a variety of state-of-the-art bioanalytical techniques to investigate detection-sensitivity issues for a range of terrestrial microbiota biomarkers obtained from so-called "hostile" environments. The philosophy is not to characterize the microbial ecology in these sites, but rather to detect biomolecules and remnants of life. It therefore becomes irrelevant what DNA is being detected (as long as it can be differentiated from a known contaminant); detection of DNA, RNA, proteins, and ATP are an indicator of life in these environments. Specifically, Steele will assay samples using the techniques listed below, from Yellowstone hot springs, USA (in collaboration with M. Schweitzer, Montana State University), the acidic Rio Tinto, Spain (in collaboration with V. Parro Garcia and C. Briones at the Centro de Astrobiología, Spain), wall rock from deep-sea hydrothermal vent chimneys on the Juan de Fuca Ridge (in collaboration with Co-I Baross and D. Kelly, University of Washington), Mars desert research station, Haughton crater (in collaboration with C. Cockell, British Antarctic Survey), and Lake Tanganika sediments, a site of continental sub-aquatic hydrothermal vents (with Co-I Scott). Many of these samples are already in our possession, and other sample sets of relevance to Solar System exploration will be sought.

Co-Is Steele and Vicenzi and Collaborator Toporski will also explore whether bioanalytical techniques can be applied to detect evidence of ancient life from various fossil localities (see **Section 5.7**). Some of the best-preserved organic fossils (including those of bacterial mats) are from the Enspel Formation in Germany. These ~ 25-Ma old rocks contain fossils spanning a wide range of mono- and multi-cellular organisms. Preliminary analyses (with ToF-SIMS, GC-MS and DNA extraction, SELDI-ToF antihopane and PAH antibodies) reveals a considerable array of well-preserved biomarkers. Thus the Enspel Formation may be an optimum fossil locality (along with the Messel and Wilershausen oil shales) to test bioanalytic strategies for the detection of ancient life (Toporski et al. 2002a). Also of considerable interest to the astrobiological community are organic fossils contained within some of the most ancient terrestrial sediments, i.e., the Archaean deposits and red sandstones of Western Australia. These extremely ancient rocks will likely prove to be the most difficult samples in which to detect *bona fide* chemical biosignatures. In collaboration with M. Brasier at Oxford University we will seek to address the ambiguity of the reported microfossils within the Warrawoona Group using the suite of techniques outlined below.

A suite of Martian and carbonaceous meteorites in Co-I Steele's possession will be assayed for any terrestrial contamination that may have occurred over many years of storage. Co-I Steele will apply site-specific molecular probes and imaging techniques to identify and distinguish terrestrial contamination from endogenous organics in this suite along with new material in complementary experiments including those of Co-Is Alexander, Cody, and Nittler. These experiments will bear on future curatorial strategies as well as help us to assess whether there exists a substantial fraction of terrestrial organic matter that could complicate our evaluation of cosmochemical organic inventories.

Each sample locality or experiment chosen poses a unique set of scientific challenges. This research task is designed to begin to set terrestrial baseline signatures for instruments that are currently being developed for Mars exploration for detection of both viable and fossil life. For this study we will apply a broad array of analytical techniques to augment and refine the bioanalytical methods currently used. Although most of these methods will not be part of any spacecraft science instrumentation package for the foreseeable future, all will serve to optimize the select subset of instruments that are ultimately chosen for the purpose of extraterrestrial life detection or sample return. The methods we will employ include the following:

Imaging. We will make use of fluorescence and light microscopy, scanning electron microscopy (CIW), soft X-ray (C, N, O) chemical imaging (in collaboration with Co-I Cody and Collaborator Ade at the Advanced Light Source, ALS), atomic force microscopy (AFM, Montana State University), and chemical force microscopy (Montana State University). This last technique uses an antibody attached to the silicon nitride tip of an atomic-force-microscopy cantilever to detect an antigen to the antibody binding (Mazzola et al. 1999). This information is combined with a 3D topographic image of the surface afforded by standard AFM protocols. We will explore the use of nano-size gold particles attached to secondary marker antibodies to localize the initial antibody reaction (available from Molecular Probes, Inc.) and image these reactions using field emission SEM and TEM (Vali et al. 2001). Finally, we will explore the utility of near-field scanning optical microscopy that will allow for direct visualization of target objects with spatial resolutions well below the diffraction limits of conventional optics (under development in collaboration with Co-I Nittler as part of a project funded by the NASA Sample Return Laboratory Instruments and Data Analysis Program).

Spectroscopy. We will apply micro-Raman (CIW) and synchrotron-based micro-infrared spectroscopy (National Synchrotron Light Source, NSLS), XANES of carbon, nitrogen, and sulfur) (NSLS and ALS), and ^{13}C solid-state nuclear magnetic resonance spectroscopy (CIW) (of demineralized samples) for quantitative analysis of total organic carbon functionality.

Spectrometry. We will apply time-of-flight secondary ion mass spectrometry (ToF-SIMS, see **Section 5.7**), surface enhanced laser desorption ionization (SELDI) mass spectrometry (CIW), as well as conventional GC-MS (CIW).

Bioanalysis. At CIW we will apply real-time polymerase chain reaction (RT-PCR) using common primers to study the effect of mineralization on the amount of DNA that can be recovered from viral and bacterial species that are deliberately fossilized and that are recovered from both recent and ancient materials. The Cepheid system will yield semi-quantitative PCR, providing an assessment of the decay in detection rates of DNA with diagenesis. We will employ enzyme assays, both LAL and detection of ATP. We will explore the use of capillary electrophoresis coupled with laser fluorescence detection for extractible DNA, RNA, and proteins. We will design and test protein and DNA microarrays, as well as use commercially available DNA chips, to assay changes in bacteria during fossilization. In addition we will test our limits of detection and selectivity using flow cytometry and enzyme-linked immunosorbant assays (ELISA).

Completion of the experiments described above will provide results that can optimize the choice of techniques for a bioanalytical life-detection science package designed for future lander missions to Mars and other appropriate Solar System bodies. From the outset we envision a versatile, small-footprint instrument based on the design principle of the Modular Assay for Solar System Exploration (MASSE), under development in collaboration with D. McKay at JSC and colleagues at the Centro de Astrobiología, Spain. Specifically, the MASSE instrument concept uses microchip-based microfluidics to accept, extract, concentrate, filter, buffer, and process organic molecules of interest from a single, small sample-handling chamber. The prototype MASSE study was initially funded by NASA (2005 Mars opportunity), and it has been recommended for further development by ESA. In its current stage of development this instrument has achieved its essential proof-of-concept goals, but considerable refinement is required before this instrument can fly. Many of the analytical refinements are best done under the auspices of NASA’s Astrobiology Program, to ensure the greatest input from the large community of biologists, chemists, physicists, and engineers with a commitment toward missions designed to search for extraterrestrial life.

5.9 Management Plan

A key feature of our proposed NAI research plan is a broadly integrated approach that draws on the expertise of a team of researchers in astronomy, biology, chemistry, and Earth sciences. This section describes how the activities of researchers from these different disciplines and several widely-separated geographic locations will be integrated, both within our team and into the larger arena of the NAI virtual institute.

5.9.1 Executive Committee

Our team will be managed by an eight-member Executive Committee, consisting of Co-Investigator representatives from the consortium's institutional partners and chaired by the Principal Investigator. The initial membership will consist of John Baross from the School of Oceanography at the University of Washington, David Deamer from the Department of Biochemistry at the University of California, Santa Cruz, Alan Boss from the Department of Terrestrial Magnetism of the Carnegie Institution of Washington, Noreen Tuross from the Smithsonian Institution, George Cody from the Geophysical Laboratory of the Carnegie Institution, James Farquhar from the Department of Geology, University of Maryland, Jay Brandes from the Department of Marine Sciences, the University of Texas, and Sean Solomon from the Department of Terrestrial Magnetism of the Carnegie Institution, who will act as committee chair. Over the five-year lifetime of the project, other team members will rotate onto the Executive Committee at regular intervals. The Executive Committee will meet on a monthly basis, in face-to-face sessions where possible by virtue of appropriately timed workshops, symposia, and other multi-purpose travel opportunities, and via teleconference otherwise.

Our team benefits not only from CIW's record as an NAI lead institution for the past five years, but also from having members with management experience appropriate for guiding and coordinating such an endeavor. Principal Investigator Sean Solomon is the Director of the Carnegie Institution's Department of Terrestrial Magnetism. A past President of the American Geophysical Union, he has led multidisciplinary scientific endeavors ranging from oceanographic expeditions to explore mid-ocean ridges to the MESSENGER mission to orbit the planet Mercury.

5.9.2 Plan for multi-institutional cooperation

While most of the research described in this proposal will be conducted at the Carnegie Institution's Washington, D.C., campus, the site of both the Geophysical Laboratory and the Department of Terrestrial Magnetism, the contributions of Co-Investigators at George Mason University, the Naval Research Laboratory, the Smithsonian Institution, the University of California at Santa Cruz, the University of Maryland at College Park, the University of Texas at Austin, and the University of Washington are critical to the success in this endeavor. Our challenge, therefore, is to coordinate work at eight institutional locations. Experience has taught us that regular electronic interactions among all consortium members, as well as frequent multi-day intersite visits and longer personnel exchanges, are essential to achieve our objectives. To this end, our plan for multi-institutional cooperation consists of the following elements:

NAI Team Symposia. The Carnegie Institution's Washington, D.C., campus is centrally located in the nation's capital. We are, for example, within a few miles of NASA Headquarters, the NASA Goddard Space Flight Center, the Naval Research Laboratory, the Smithsonian Institution National Museum of Natural History and Air and Space Museum, the headquarters of the United States Geological Survey, the National Science Foundation, the National Institutes of Health, the National Academy of Sciences, and the headquarters of numerous other government agencies and scientific societies, including the American Geophysical Union, the American Chemical Society, the American Physical Society, and the American Association for the Advancement of Science. George Mason University and the University of Maryland are short drives from the Carnegie Institution campus, enabling frequent visits. Co-Investigators Deamer from the University of California, Baross from the University of Washington, and Brandes from the University of Texas all plan to make several trips per year to the area, and all have visited CIW laboratories at least once during the past 12 months.

In order to take full advantage of Carnegie's convenient location and to reduce the costs of transportation and lodgings, we will hold most of our consortium's symposia and Executive Committee meetings at Carnegie Institution facilities. (Committees of NASA, AGU, and other organizations frequently take advantage of the Broad Branch Road facility for their organizational meetings.)

In the first year, as we define and integrate our new and larger NAI team, we propose to sponsor one research and planning symposium for all of our consortium participants. The meeting will be open to others, including representatives of other NAI teams, but the focus of the symposium will be our own team's research agenda. We anticipate that this meeting will result in new collaborative links within the NAI structure. The first symposium will be held at the Carnegie Institution.

In each succeeding year we plan at least one dedicated symposium for all members of the team, held either at CIW or at another partner institution (and tied to an appropriate national meeting, if possible, to reduce travel costs). All of our symposia will be conducted in the style and spirit of Gordon Conferences, with time divided between lecture-style presentations, group discussions, and one-on-one interactions.

Intersite visits. In addition to the above symposia, we propose to sponsor numerous intersite visits during the five years of this program. These intersite visits will be of three types:

a. Lecture visits. We will sponsor an active lecture program. Each Co-Investigator, NAI Postdoctoral Fellow (in his or her second year), and NAI predoctoral fellow (near completion of the Ph.D.) will be encouraged to deliver scientific research lectures at the other partner institutions.

b. Senior staff research exchanges. When appropriate to accomplish our team's research objectives, we will sponsor site exchanges for research collaboration. Several such exchanges are mentioned in connection with specific research tasks above.

c. Junior staff exchanges. All NAI Postdoctoral and Predoctoral Fellows will be encouraged to spend at least one month visiting and engaging in research at one of the other NAI institutions. For example, a Postdoctoral Fellow in organic geochemistry at the Carnegie Institution might visit the University of Washington to collect and study samples from an ocean vent system. We believe that such exchanges will greatly enhance the professional breadth of our young colleagues, while also strengthening ties within the team.

Electronic interactions. Members of the team are already in frequent electronic contact. Information exchange will be facilitated by the new CIW NAI Website (see **Section 7.8**). A major goal of our team's IT initiative (**Section 7.8**) will be to develop the tools that best meet the interactive needs of team members for each of our collaborative research tasks.

5.9.3 Roles and responsibilities of each participant

Following are the key participants in our project and their roles in this consortium effort. Each of these individuals has endorsed the objectives and research plan described herein, and each has committed to taking on the responsibilities given below. Further details on the background and expertise of each of these participants can be found in **Section 9**. Copies of the letters of commitment from all Co-Investigators and a number of Collaborators are in **Section 13**. In the list below, the Geophysical Laboratory and the Department of Terrestrial Magnetism of the Carnegie Institution of Washington are denoted by the abbreviations GL-CIW and DTM-CIW, respectively.

- **Conel M. O'D. Alexander** (Research Staff Member, DTM-CIW) is a cosmochemist and is a supervisor of the Carnegie ion microprobe, with which he studies meteorites. Alexander will coordinate research on meteorite organic material, as well the characteristics of hydrothermal activity in meteorite parent bodies.
- **John A. Baross** (Professor, School of Oceanography, University of Washington) is a microbiologist who studies the physical and chemical environment and microbial biology of ocean hydrothermal vent systems. He will provide critical expertise on natural hydrothermal environments.
- **Nabil Boctor** (Consultant, GL-CIW) is geochemist and an expert of transition-metal sulfides. He provides a theoretical understanding of sulfide formation and reactivity, and he provides well-characterized synthetic sulfides for our experiments.
- **Alan P. Boss** (Research Staff Member, DTM-CIW) is an astrophysicist who models the collapse of molecular cloud cores and the formation of stars and planets. He will study the origins and distribution of volatiles in planetary systems.
- **R. Paul Butler** (Research Staff Member, DTM-CIW) is an astronomer who collaborates closely with Co-Is Boss, Seager, and Weinberger in assessing the modes of giant planet distributions and the probable influence of such distributions on the galactic distribution of habitable worlds.
- **Jay A. Brandes** (Co-I, University of Texas, Austin) is a marine chemist who is conducting experiments on the hydrothermal origins and isotopic signatures of abiotically synthesized reduced nitrogen and amino acids.
- **George D. Cody** (Research Staff Member, GL-CIW) is an organic geochemist who is studying rates and pathways of hydrothermal organic synthesis related to protometabolism. He will continue to guide this experimental program as well as contribute to the work on biosignatures and extraterrestrial materials using scanning transmission X-ray microscopy.
- **David Emerson** (Research Scientist, American Type Culture Collection, George Mason University) is a microbiologist who is investigating Fe-oxidizing lithotrophic procaryotes. He will continue to study metabolic processes in these organisms, while coordinating the sampling, archiving, and distribution of type microbial specimens to NAI members.
- **David W. Deamer** (University of California, Santa Cruz) is a biochemist who will coordinate sampling of hot springs and subsequent analysis at CIW. He will collaborate with prebiotic chemistry initiatives at CIW in lipid encapsulation experiments.
- **James Farquhar** (University of Maryland, Department of Geology) is a stable isotope geochemist and will participate in the research related to the Earth's earliest sulfur cycle as well as provide expertise in sulfur isotopic analysis.
- **Marilyn L. Fogel** (Research Staff Member, GL-CIW) is a biologist and will collaborate in the analysis of stable isotopic fractionation in biotic and abiotic processes and the application of SELDI-ToF for proteomics in collaboration with studies of life in extreme environments.
- **Erik H. Hauri** (Research Staff Member, DTM-CIW) is a geochemist who will provide measurements of Fe isotopes to integrate with the studies on iron-oxidizing bacteria with Co-I Emerson.
- **Robert M. Hazen** (Research Staff Member, GL-CIW) is an experimental mineralogist with expertise in high-temperature, high-pressure apparatus. He will participate in research related to the origins of chirality, biosignatures, and mineral-mediated organic synthesis, and he will engage in extensive public outreach and education activities.
- **Russell J. Hemley** (Research Staff Member, GL-CIW) is a physical chemist who has developed spectroscopic methods for high-pressure research. He will coordinate studies that employ hydrothermal diamond-window devices for real-time spectroscopic analysis of organic synthesis and bacterial metabolism under extreme conditions.
- **Wesley T. Huntress** (Director, GL-CIW) is a chemical physicist and will collaborate with the extraterrestrial materials research group by providing insight into chemical dynamics and ion-molecule reactions.

- **Karl Kehm** (Collaborator, Washington College) is a geochemist and will measure iron isotopes in natural and laboratory samples in an effort to characterize and understand the various processes, both biotic and abiotic, that can induce iron isotopic mass fractionation. These studies will help determine whether iron isotopes are a useful biomarker.
- **Timothy J. McCoy** (Smithsonian Institution) is a cosmochemist and will collaborate on studies of the fate of carbon during planetary differentiation and the relationship between such processes and the chemistry of the early Earth.
- **Larry R. Nittler** (Research Staff Member, DTM-CIW) is a cosmochemist who will explore the organic chemistry of IDPs as part of the extraterrestrial materials research initiative.
- **Shuei Ono** (Postdoctoral Fellow, GL-CIW) is a geochemist and will participate in the research related to the Earth's earliest sulfur cycle providing expertise in sulfur isotopic analysis. He will focus on the development of ultra-low blank methods and methods for the analysis of organic sulfur.
- **Douglas Rumble III** (Research Staff Member, GL-CIW) is a stable isotope geochemist and will lead the research on the Earth's earliest sulfur cycle. He provides expertise in sulfur isotopic analysis and will conduct field studies in the Archean basins of Western Australia.
- **Sara Seager** (Research Staff Member, DTM-CIW) is an astronomer and will model carbon and water in extrasolar planetary atmospheres. Specifically she will investigate the temperature-diagnostic potential of carbon in giant planet atmospheres as well as develop giant planet metallicity indicators based on carbon and water atmospheric spectral features.
- **James H. Scott** (Research Staff Member, GL-CIW) is a microbiologist and will focus on stress adaption of microorganisms under extreme conditions. He will develop and use molecular biological methods to ascertain global regulation in response to pressure.
- **Anurag Sharma** (Postdoctoral Fellow, GL-CIW) is a geochemist and will collaborate on experiments involving life in extreme environments as well as provide expertise in hydrothermal diamond-anvil-cell studies related to life in extreme environments.
- **Sean C. Solomon** (Director, DTM-CIW) is a planetary scientist who has spent more than 30 years investigating mid-ocean ridges in the Earth's oceans and the thermal and magmatic evolution of planets and satellites. In addition to providing overall leadership to the consortium, he will explore the range of possible Solar System environments of present and past hydrothermal systems.
- **Andrew Steele** (Research Staff Member, GL-CIW) is a molecular biologist who will develop and apply methods in biotechnology to address astrobiological questions related to biosignatures and life in extreme environments.
- **Rhonda Stroud** (Research Staff Member, Naval Research Laboratory) is a physicist who will conduct high-resolution analytical transmission electron microscopy studies at the NRL of carbon-bearing phases in interstellar dust particles and meteorites and of fossilized bacterial and viral material in collaborations with Co-Is Alexander, Nittler, and Steele.
- **Jan Toporski** (Postdoctoral Fellow, GL-CIW) is a microbiologist who will participate in biomineralization studies of microbes and viruses as part of the biosignatures research effort. He will continue studies of the ancient bacterial mats in the Enspel Formation, Germany.
- **Noreen C. Tuross** (Smithsonian Institution) is a biochemist who will provide expertise in bioanalytical methods for the detection of biosignatures in the Enspel Formation, Germany. She will also study the preservation of molecular biosignatures in stromatolites.
- **Edward P. Vicenzi** (Smithsonian Institution) is a geochemist who will provide expertise and analytical collaboration in the use of time-of-flight secondary ion mass spectrometer (ToF-SIMS) for applications in biosignatures research and extraterrestrial materials.
- **Alycia J. Weinberger** (Research Staff Member, DTM-CIW) is an infrared astronomer who will integrate observations of extrasolar disks to bridge to models of planet formation made by our astronomical theorists as well as make observational connections to our research on extraterrestrial materials.
- **George W. Wetherill** (Director Emeritus, DTM-CIW) is a planetary scientist who performs numerical simulations of planet formation. He will continue his investigation of the origin

and distribution of Earth-like planets and implications for volatiles on other planets and satellites.

- **Hatten S. Yoder, Jr.** (Director Emeritus, GL-CIW) is an experimental petrologist who supervises the gas-media high-pressure laboratory used for hydrothermal synthesis experiments.

6. References

Abeles, R. H., Frey, P. A. & Jencks, W. P. (1992). *Biochemistry*. Boston: Jones and Bartlet Publishers, 838 pp.

Aléon, J., Engrand, C., Robert, F. & Chaussidon, M. (2001). Clues to the origin of interplanetary dust particles from the isotopic study of their hydrogen-bearing phases. *Geochimica et Cosmochimica Acta* 65: 4399-4412.

Allamandola, L. J., Hudgins, D. M. & Sandford, S. A. (1999). Modeling the unidentified infrared emission with combinations of polycyclic aromatic hydrocarbons. *Astrophysical Journal* 511: L115-L119.

Anders, E. (1989). Pre-biotic organic matter from comets and asteroids. *Nature* 342: 255-57.

Apel, C. L., Deamer, D. W. & Mautner, M. (2002). Self-assembled vesicles of monocarboxylic acids and alcohols: Conditions for stability and for the encapsulation of biopolymers. *Biochimica et Biophysica Acta* 1559: 1-10.

Arrhenius, G., Gedulin, B. & Mojzsis, S. (1993). Phosphate models for chemical evolution. In: C. Ponnamperuma & J. Chela-Flores (Eds.). *Chemical Evolution: Origin of Life* (pp. 23-40). New York: A. Deepak Publishing.

Auroux, J. (2002). Micro total analysis systems. 2. Analytical standard operations and applications. *Analytical Chemistry* 74: 2637-2652.

Avetisov, V. A. (1999). Origin of biological homochirality: Directed selection or random motion? In G. Pályi, C. Zucchi & L. Caglioti (Eds.). *Advances in Biochirality* (pp. 69-84). New York: Elsevier.

Avetisov, V. A., Goldanskii, V. I. & Kuz'min, V. V. (1991). Handedness, origin of life and evolution. *Physics Today* 44: 33-41.

Bailey, J., Chrysostomou, A., Hough, J. H., Gledhill, T. M., McCall, A., Clark, S., Menard, F. & Tamura, M. (1998). Circular polarization in star-formation regions: Implications for biomolecular homochirality. *Science* 281: 672-674.

Bangham, A.D., Standish, M. M. & Watkins, J. B. (1965). Diffusion of univalent ions across the lamellae of swollen phospholipids. *Journal of Molecular Biology* 13: 238-252.

Barghoorn, E. S. and Tyler, S. A. (1965). Microfossils from the Gun Flint Chert. *Science* 147: 563-577.

Basinger, J. F. (1981). The vegetative body of Metasequoia milleri from the middle Eocene of southern British Columbia. *Canadian Journal of Botany* 59: 2379-2410.

Beichman, C. A., Woolf, N. J. & Lindensmith, C. A. (1999). *The Terrestrial Planet Finder: A NASA Origins Program to Search for Habitable Planets* (158 pp.). Pasadena: Jet Propulsion Laboratory.

Bernal, J. D. (1951). *The Physical Basis of Life*. London: Routledge and Kegan Paul.

Bernstein, M. P., Dworkin, J. P., Sandford, S. A., Cooper, G. W. & Allamandola, L. J. (2002). The formation of racemic amino acids from the ultraviolet photolysis of interstellar ice analogues. *Nature* 416: 401-403.

Bernstein, M. P., Sandford, S. A., Allamandola, L. J., Chang, S. & Scharberg, M. A. (1995). Organic compounds produced by photolysis of realistic interstellar and cometary ice analogs containing methanol. *Astrophysical Journal* 454: 327-344.

Blank, J., Miller, G. H., Ahrens, M. J. & Winans, R. E. (2001). Experimental shock chemistry of aqueous amino acid solutions and the cometary delivery of prebiotic compounds. *Origins of Life and Evolution of the Biosphere* 31: 15-51.

Boctor, N. Z., Alexander, C. M. O'D., Wang, J. & Hauri, E. H. (Submitted, 2003). Sources of water in Martian meteorites. *Geochimica et Cosmochimica Acta*.

Bolli, M., Micura, R. & Eschenmoser, A. (1997). Pyranosyl-RNA: Chiroselective self-assembly of base sequences by ligative oligomerization of tetranucleotide-2',3'-cyclophosphates (with a commentary concerning the origin of biomolecular homochirality). *Chemistry & Biology* 4: 309-320.

Bonner, W. A. (1991). The origin and amplification of biomolecular chirality. *Origins of Life and Evolution of the Biosphere* 22: 59-111.

Bonner, W. A. (1992). Terrestrial and extraterrestrial sources of molecular homochirality. *Origins of Life and Evolution of the Biosphere* 21: 407-420.

Bonner, W. A. (1995). Chirality and life. *Origins of Life and Evolution of the Biosphere* 25: 175-190.

Bonner, W. A., Kavasmaneck, P. R., Martin, F. S. & Flores, J. J. (1974). Asymmetric adsorption of alanine by quartz. *Science* 186: 143-144.

Bonner, W. A., Kavasmaneck, P. R., Martin, F. S. & Flores, J. J. (1975). Asymmetric adsorption by quartz: A model for the prebiotic origin of optical activity. *Origin of Life* 6: 367-376.

Boss, A. P. (1997). Giant planet formation by gravitational instability. *Science* 276: 1836-1839.

Boss, A. P., Wetherill, G. W. & Haghighipour, N. (2002). Rapid formation of ice giant planets. *Icarus* 156: 291-295.

Boyce, C. K., Cody, G. D., Feser, M., Jacobsen, C., Knoll, A. H. & Wirick, S. (2002). Organic chemical differentiation within fossil plant cell walls detected with X-ray spectromicroscopy. *Geology* 30: 1039-1042.

Boyce, C. K., Hazen, R. M. & Knoll, A. H. (2001). Nondestructive, in situ, cellular-scale mapping of elemental abundances including organic carbon in permineralized fossils. *Proceedings of the National Academy of Sciences* 98: 5970-5974.

Bradley, J. P., Sandford, S. A. & Walker, R. M. (1988). Interplanetary dust particles. In: J. F. Kerridge and M. S. Matthews (Eds.). *Meteorites and the Early Solar System* (pp. 861-895). Tucson: University of Arizona Press.

Bradley, J. P., Keller, L. P., Snow, T. P., Hanner, M. S., Flynn, G. J., Gezo, J. C., Clemett, S. J., Brownlee, D. E. & Bowey, J. E. (1999). An infrared spectral match between GEMS and interstellar grains. *Science* 285: 1716-1718.

Brandes, J. A., Boctor, N. Z., Hazen, R. M., Yoder, H. S., Jr. & Cody, G. D. (2000). Early pre- and post-biotic synthesis of alanine: An alternative to the Strecker synthesis. In: G. A. Goodfriend, M. J. Collins, M. L. Fogel, S. A. Macko & J. F. Wehmiller (Eds.). *Perspectives in Amino Acid and Protein Geochemistry*. (pp. 41-47). New York: Oxford University Press.

Brandes, J. A., Cody, G. D., Hazen, R. M. & Yoder, H. S., Jr. (2001). Stability and transformations of nitrogenous compounds under hydrothermal conditions. *Astrobiology* 1: 298 (abstr.).

Brasier, M. D., Green, O. R., Jephcoat, A. P., Kleppe A. K., van Kranendonk, M. J., Lindsay, J. F., Steele, A. & Grassineau, N. V. (2002). Earth's oldest fossils: Questioning the evidence. *Nature* 416: 76-81.

Brocks, J. J., Logan, G. A., Buick, R. and Summons, R. E. (1999). Archaean molecular fossils and the early rise of eukaryotes. *Science* 285: 1033-1036.

Brooks, J. M., Anderson, A. L., Sassen, R., Macdonald, I., Kennicutt, M. C. K., II & Guinasso, N. L., Jr. (1994). Hydrate occurrences in shallow subsurface cores from continental slope sediments. In: E. D. Sloan, J. Happle & M. A. Hnatow (Eds.). *International Conference on Natural Gas Hydrates* (pp. 381-391). New York Academy of Sciences.

Brown, M. E. & Calvin, W. M. (2000). Evidence for crystalline water and ammonia ices on Pluto's Satellite Charon. *Science* 287: 107-109.

Burrrows, A., Hubbard, W. B., Lunine, J. I. & Liebert, J. (2001). The theory of brown dwarfs and extrasolar giant planets. *Reviews of Modern Phys*ics 73: 719-765.

Butler, R. P., Marcy, G. W., Vogt, S. S., Fischer, D. A., Henry, G. W., Laughlin, G. & Wright, J. T. (2003). Seven new Keck planets orbiting G and K dwarfs. *Astrophysical Journal* 582: 455-466.

Cady, S. L. & Farmer, J. D. (1996). Fossilization processes in siliceous thermal springs: Trends in preservation along thermal gradients. In: G. R. Brock & J. A. Goode (Eds.). *Evolution of Hydrothermal Ecosystems on Earth (and Mars?)*, *Ciba Foundation Symposium 202* (pp. 150-173). Chichester: Whiley.

Chakrabarti, A. & Deamer, D.W. (1994). Permeation of membranes by the neutral form of amino acids and peptides: Relevance to the origin of peptide translocation. *Journal of Molecular Evolution* 39:1-5.

Chakrabarti, A., Breaker, R. R., Joyce, G. F. & Deamer, D. W. (1994). Production of RNA by a polymerase protein encapsulated within phospholipid vesicles. *Journal of Molecular Evolution* 39: 555-559.

Chambers, J. E. & Wetherill, G. W. (2001). Planets in the asteroid belt. *Meteoritics and Planetary Science* 36: 381-400.

Chela-Flores, J. (1994). The origin of chirality in protein amino acids. *Chirality* 6: 165-168.

Chyba, C. F. & Sagan, C. (1992). Endogenous production, exogenous delivery and impact-shock synthesis of organic molecules: An inventory for the origin of life. *Nature* 355: 125-132.

Cintas, P. (2002). Chirality of living systems: A helping hand from crystals and oligopeptides. *Angewault Chemie International Edition* 41: 1139-1145.

Clark, R. N. (1980). Ganymede, Europa, Callisto, and Saturn's rings - Compositional analysis from reflectance spectroscopy. *Icarus* 44: 388-409.

Clark, S. (1999). Polarized starlight and the handedness of life. *American Scientist* 87: 336-343.

Clemett, S. J., Maechling, C. R., Zare, R. N., Swan, P. D. & Walker, R. M. (1993). Identification of complex aromatic molecules in individual interplanetary dust particles. *Science* 262: 721-725.

Clemett, S. J., Messenger, S., Thomas-Keprta, K. L., Wentworth, S. J., Robinson, G. A. & McKay, D. S. (2002). Spatially resolved analysis of amines using a fluorescence molecular probe: molecular analysis of IDPs. *Lunar and Planetary Science* XXXIII: #1898 (abstr.).

Cloud, P. E. (1965). Significance of the Gun Flint (Precambrian) microflora. *Science* 148: 27-35.

Cody, G. D., (2000). Probing chemistry within the membrane structure of wood with soft X-ray spectral microscopy. In: W. Meyer-Ilse and T. Warwick (Eds.). *X-ray Microscopy: Proceedings of the Sixth International Conference* (pp. 307-312). New York: American Institute of Physics.

Cody, G. D., Ade, H., Behal, S., Botto, R. E, Disko, M., Kirz, J. & Wirick, S. C. (1995a). NEXAFS microanalysis and imaging of a bituminous coal. *Energy & Fuels* 9: 75-83.

Cody, G. D., Ade, H., Behal, S., Botto, R. E., Disko, M., Kirz, J. & Wirick, S. C. (1995b). Inner shell spectroscopy and imaging of a subbituminous coal: In-situ analysis of organic and inorganic microscostructure using C(1s)-, Ca(2p)-, and Cl(2s)-NEXAFS. *Energy & Fuels* 9: 525-533.

Cody, G. D., Alexander, C. M. O'D. & Tera, F. (2002). Solid state (^{1}H and ^{13}C) NMR spectroscopy of the insoluble organic residue in the Murchison meteorite: A self-consistent quantitative analysis. *Geochimica et Cosmochimica Acta* 66: 1851-1865.

Cody, G. D., Alexander, C. M. O'D. & Tera, F. (2003a). Compositional trends in chondritic organic solids across and between meteoritic groups. *Lunar and Planetary Science* XXXIV: #1822 (abstr.).

Cody, G. D., Boctor, N. Z., Filley, T. R., Hazen, R. M., Scott, J. H., Sharma, A. & Yoder, H. S., Jr. (2000). The primordial synthesis of carbonylated iron-sulfur clusters and the synthesis of pyruvate. *Science* 289: 1339-1341.

Cody, G. D., Boctor, N. Z., Hazen, R. M., Brandes, J. A., Morowitz, H. J. & Yoder, H. S., Jr. (2001). Geochemical roots of autotrophic carbon fixation: Hydrothermal experiments in the system citric acid-H_2O-(±FeS)-(±NiS). *Geochimica et Cosmochimica Acta* 65: 3557-3576.

Cody, G. D., Boctor, N. Z., Brandes, J. A., Filley, T. R., Hazen, R. M. & Yoder H. S., Jr. (Submitted, 2003b). Assaying the catalytic potential of transition metal sulfides for geochemical carbon fixation. *Geochimica et Cosmochimica Acta.*

Cody, G. D., Boctor, N. Z., Brandes, J. A., Hazen, R. M. & Yoder, H. S. (2003c). Carbon and nitrogen fixation strategies of a young terrestrial planet. *NASA Astrobiology Institute General Meeting 2003:* 445-446 (abstr.).

Cody, G.. D., Botto, R. E., Ade, H. & Wirick, S. (1996). The application of soft X-ray microscopy to the in-situ analysis of sporinite in coal. *International Journal of Coal Geology* 32: 69-86.

Collinson, M. E., Mösle, B., Finch, P., Scott, A. C. & Wilson, R. (1998). The preservation of plant cuticle in the fossil record: A chemical and microscopical investigation. *Ancient Biomolecules* 2: 251-265.

Costard, F., Forget, F., Mangold, N. & Peulvast, J. P. (2002). Formation of recent Martian debris flows by melting of near-surface ground ice at high obliquity. *Science* 295: 110-113.

Cronin, J. R. & Pizzarello, S. (1997). Enantiomeric excesses in meteoritic amino acids. *Science* 275: 951-955.

Cronin, J. R., Pizzarello, S. & Cruikshank, D. P. (1988). Organic matter in carbonaceous chondrites, planetary satellites, asteroids and comets. In: J. F. Kerridge and M. S. Matthews (Eds.). *Meteorites and the Early Solar System* (pp. 819-860). Tucson: University of Arizona Press.

Cruikshank, D. P., Pilcher, C. B. & Morrison, D. (1976). Pluto - Evidence for methane frost. *Science* 194: 835-837.

Dana, E. S. (1949). *A Textbook of Mineralogy.* New York: John Wiley & Sons.

Davankov, V. A. (1997). The nature of chiral recognition: Is it a three-point interaction? *Chirality* 9: 99-102.

Deamer, D. W. (1985). Boundary structures are formed by organic components of the Murchison carbonaceous chondrite. *Nature* 317: 792-794.

Deamer, D. W. (1997). The first living systems: A bioenergetic perspective. *Microbiology and Molecular Biology Review* 61: 230-261.

Deamer, D. W. & Barchfeld, G. L. (1982). Encapsulation of macromolecules by lipid vesicles under simulated prebiotic conditions. *Journal of Molecular Evolution* 18: 203-206.

Deamer, D. W. & Pashley, R. M. (1989). Amphiphilic components of carbonaceous meteorites. *Origins of Life and Evolution of the Biosphere* 19: 21-33.

Deamer, D. W., Dworkin, J. P., Sandford, S. A., Bernstein, M. P. & Allamandola, L. J. (2003). The first cell membranes. *Astrobiology* 2: 371-381.

De Duve, C. (1991). *Blueprint for a Cell*. Burlington: Neil Patterson.

Dobson, C. M., Ellison, G. B., Tuck, A. & Vaida, V. (2000). Atmospheric aerosols as prebiotic chemical reactors. *Proceedings of the National Academy of Sciences* 97: 11864-11868.

Doukov, T. I., Iverson, T. M., Seravalli, J., Ragsdale, S. W. & Drennen C. L. (2002). A Ni-Fe-Cu center in a bifunctional carbon monoxide dehydrogenase/acetyl-CoA synthase. *Science* 298: 567-571.

Dworkin, J. P., Deamer, D. W., Sandford, S. A. & Allamandola, L. J. (2001). Self-assembling amphiphilic molecules: Synthesis in simulated interstellar/precometary ices. *Proceedings of the National Academy of Sciences* 98: 815-819.

Eckert, C. J., Peachey, N. M., Swanson, D. R., Takacs, J. M., Khan, M. A., Gong, X., Kim, J.-H., Wang, J. & Uphaus, R. A. (1993). Separation of chiral phases in monolayer crystals of racemic amphiphiles. *Nature* 362: 614-616.

Ehrenfreund, P., Irvine, W., Becker, L., Blank, J., Brucato, J. R., Colangeli, L., Derenne, S., Despois, D., Dutrey, A., Fraaije, H., Lazcano, A., Owen, T. & Robert, F. (2002). Astrophysical and astrochemical insights into the origin of life. *Reports on Progress in Physics* 65: 1427-1487.

Eiler, J. M., Kitchen, N., Leshin, L. & Strausberg, M. (2002). Hosts of hydrogen in Allan Hills 84001: Evidence for hydrous Martian salts in the oldest Martian meteorite? *Meteoritics and Planetary Science* 37: 395-405.

Emerson, D. & Moyer, C. (1997). Isolation and characterization of novel iron-oxidizing bacteria that grow at circumneutral pH. *Applied and Environmental Microbiology* 63: 4784-4792.

Engel, M. H. & Macko, S. A. (1997). Isotopic evidence for extraterrestrial non-racemic amino acids in the Murchison meteorite. *Nature* 389: 265-268.

Engel, M. H. & Nagy, B. (1982). Distribution and enantiomeric composition of amino acids in the Murchison meteorite. *Nature* 296: 837-840.

Ertem, G. & Ferris, J. P. (1996). Synthesis of RNA oligomers on heterogeneous templates. *Nature* 379: 238-240.

Ertem, G. & Ferris, J. P. (1997). Template-directed synthesis using the heterogeneous templates produced by montmorillonite catalysis. A Possible bridge between the prebiotic and RNA worlds. *Journal of the American Chemical Society* 119: 7197-7201.

Evgenii, K. & Wolfram, T. (2000). The role of quartz in the origin of optical activity on Earth. *Origins of Life and Evolution of the Biosphere* 30: 431-434.

Fani, R., Gallo, R. & Lio. P., (2000). Molecular evolution of nitrogen fixation: The evolutionary history of the nifD, nifK, nifE, and nifN genes. *Journal of Molecular Evolution* 51: 1-11.

Farquhar, J., Bao, H. & Thiemens, M. H. (2000). Atmospheric influence of Earth's earliest sulfur cycle. *Science* 289: 756-758.

Farquhar, J. & Thiemens, M. H. (2000). Oxygen cycle of the Martian atmosphere-regolith system; δ^{17}O of secondary phases in Nakhla and Lafayette. *Journal of Geophysical Research* 105: 11,991-11,997.

Fedo, C. M. & Whitehouse, M. J. (2002). Metasomatic origin of quartz-pyroxene rock, Akilia, Greenland, and implications for Earth's earliest life. *Science* 296: 1448-1452.

Ferris, J. P., Hill, A. R., Jr., Liu, R. & Orgel, L. E. (1996). Synthesis of long prebiotic oligomers on mineral surfaces. *Nature* 381: 59-61.

Flynn, G. J., Feser, M., Keller, L. P., Jacobsen, C., Wirick, S. & Avakians, S. (2001). Carbon-XANES and oxygen-XANES measurements on interplanetary dust particles: A preliminary measurement of the C to O ratio in the organic matter in a cluster IDP. *Lunar and Planetary Science* XXXII: #1603 (abstr.).

Flynn, G. J., Keller, L. P., Joswiak, D. & Brownlee, D. E. (2002). Infrared analysis of organic carbon in anhydrous and hydrated interplanetary dust particles: FTIR identification of carbonyl (C=O) in IDPs. *Lunar and Planetary Science* XXXIII: #1320 (abstr.).

Freund, F., Staple, A. & Scoville, J. (2001). Organic protomolecule assembly in igneous minerals. *Proceedings of the National Academy of Sciences* 98: 2142-2147.

Frondel, C. (1978). Characters of quartz fibers. *American Mineralogist* 63: 17-27.

Gibson, G. (2002). Microarrays in ecology and evolution: A preview. *Molecular Ecology* 11: 17-24.

Gilbert, W. (1986). The RNA world. *Nature* 319: 618-619.

Glavin, D. P., Schubert, M., Botta, O., Kminek, G. & Bada, J. L. (2001). Detecting pyrolysis products from bacteria on Mars. *Earth and Planetary Science Letters* 185: 1-5.

Golden, D. C., Ming, D. W., Schwandt, C. S., Morris, R., Yang, S.V., Lofgren, G. E. & McKay, G. A. (2000). An experimental study on kinetically-driven precipitation of calcium-magnesium-iron carbonates from solution: Implications for the low temperature formation of carbonates in Martian meteorite Allan Hills 84001. *Meteoritics and Planetary Science* 35: 457-465.

Gooding, J. L., Wentworth, S. J. & Zolensky, M. E. (1991). Aqueous alteration of the Nakhla meteorite. *Meteoritics* 26: 135-143.

Hafenbradl, D., Keller, M., Wachtershauser, G. & Stetter, K. O. (1995). Primordial amino-acids by reductive amination of alpha-oxo acids in conjunction with the oxidative formation of pyrite. *Tetrahedron Letters* 36: 5179-5182.

Hargreaves, W. R. & Deamer, D. W. (1978). Liposomes from ionic, single-chain amphiphiles. *Biochemistry* 17: 3759-3768.

Hauck, S. A., II & Phillips, R. J. (2002). Thermal and crustal evolution of Mars. *Journal of Geophysical Research* 107: 10.1029/2001JE001801.

Haythornthwaite, C. (1996). Social network analysis: An approach and technique for the study of information exchange. *Library and Information Science Research* 18 (4): 323-342.

Hazen, R. M. (2001). Emergence and the origin of life. In: G. Palyi (Ed.). *Fundamentals of Life*, (pp. 41-50). New York: Elsevier.

Hazen, R. M., Filley, T. R. & Goodfriend, G. A. (2001). Selective adsorption of L- and D-amino acids on calcite: Implications for biochemical homochirality. *Proceedings of the National Academy of Sciences* 98: 5487-5490.

Hazen, R. M. & Sholl, D. S. (2002). Origins of biomolecular homochirality: selective molecular adsorption on crystalline surfaces. *Astrobiology*. 2: 598-599.

Hazen, R. M. & Sholl, D. S. (In Press, 2003). Chiral selection on inorganic crystalline surfaces. *Nature Materials*.

Heinen, W. & Lauers, A. M. (1996). Organic sulfur compounds resulting from the interaction of iron sulfide, hydrogen sulfide and carbon dioxide in an aerobic aqueous environment. *Origins of Life and Evolution of the Biosphere* 26:131-150.

Hill, A. R., Jr., Böhler, C. & Orgel, L. E. (1998). Polymerization on the rocks: Negatively-charged β-amino acids. *Origins of Life and Evolution of the Biosphere* 28: 235-243.

Hoheisel, J. D. (1997). Oligomer chip technology. *Trends in Biotechnology* 15: 465–469.

Huang, I. (1999). Analysis of estrogenic hormones in municipal wastewater effluent and surface water using enzyme-linked immunosorbent assay and gas chromatography/tandem mass spectrometry. *Environal Toxicology and Chemistry* 20: 133-139.

Huber, C. & Wächtershäuser, G. (1997). Activated acetic acid by carbon fixation on (Fe,Ni)S under primordial conditions. *Science* 276: 245-247.

Inaba, S., Ikoma, M. & Wetherill, G. W. (Submitted, 2003a). Enhanced collision rate of a protoplanet by an atmosphere. *Icarus*.

Inaba, S., Wetherill, G. W. & Ikoma, M. (Submitted, 2003b). Formation of gas giant planets: Core accretion models with fragmentation and planetary envelope. *Icarus*.

Innes, H. E., Bishop, A. N., Head, I. M. & Farrimond, P. (1997). Preservation and diagenesis of hopanoids in recent lacustrine sediments of Priest Pot, England. *Organic Geochemistry* 26: 565-576.

Irvine, W. M., Schloerb, F. P., Crovisier, J., Fegley, B., Jr. & Mumma, M. J. (2000). Comets: A link between interstellar and nebular chemistry. In: V. Mannings, A. P. Boss & S. S. Russell (Eds.). *Protostars and Planets IV* (pp. 1159-1200). Tucson: University of Arizona Press.

Isidorov, V. A., Zenkevich, I. G., & Karpov, G.A. (1992). Volatile organic compounds in steam-gas outflows of several volcanoes and hydrothermal systems in Kamchatka. *Volcanology and Seismology* 13: 287-293.

Jacobsen, C. & Kirz, J. (1998). X-ray microscopy with synchrotron radiation: *Nature, Structural Biology* 5: 650-653.

Jull, A. J. T., Courtney, C., Jeffrey, D. A. & Beck, J. W. (1998). Isotopic evidence for a terrestrial source of organic compounds found in Martian meteorites Allan Hills 84001 and Elephant Moraine 79001. *Science* 279: 366-369.

Karagounis, G. & Coumonlos, G. (1938). A new method for resolving a racemic compound. *Nature* 142: 162-163.

Karlsson, H. R., Clayton, R. N., Gibson, E. K. & Mayeda, T. K. (1992). Water in SNC meteorites: Evidence for a Martian hydrosphere. *Science* 255: 1409-1411.

Kashefi, K., Holmes, D. F., Baross, J. A. & Lovley, D. R. (Submitted, 2003). Thermophily in the *Geobacteraceae*: *Geothermobacter ehrlichii* gen. Nov., sp. nov., a novel thermophilic *Geobacteraceae* from the “Bag City” hydrothermal vent. *International Journal of Systematic and Evolutionary Microbiology*.

Kehm, K., Hauri, E. H., Alexander, C. M. O'D. & Carlson, R. W. (In Press, 2003). High precision iron isotope measurements of meteoritic material by cold plasma ICP-MS. *Geochimica et Comochimica Acta.*

Keller, L. P., Messenger, S., Flynn, G. J., Wirick, S. & Jacobsen, C. (2002). Analysis of a deuterium hotspot in an interplanetary dust particle: Implications for the carrier of hydrogen isotopic anomalies in IDPs. *Lunar and Planetary Science* XXXIII: #1869 (abstr.).

Keller, L. P., Messenger, S., Miller, M., & Thomas, K. L. (1997). Nitrogen speciation in a N-15-enriched interplanetary dust particle. *Lunar and Planetary Science* XXVIII: 707 (abstr.).

Kidston, R. & Lang, W. H. (1920). On old red sandstone plants showing structure, from the Rhynie Chert bed, Aberdeenshire: Part III. Asteroxylon mackiei. *Royal Society of Edinburgh Transactions*, 52: 643-680.

Kissel, J. & Krueger, F. R. (1987). The organic component in dust from comet Halley as measured by the PUMA mass spectrometer on board Vega 1. *Nature* 326: 755-760.

Knoll, A.H. (1985). Exceptional preservation of photosynthetic organisms in silicified carbonates and silicified peats. *Philisophical Transactions of the Royal Society of London* 311: 11-122.

Kortenkamp, S. J., Wetherill, G. W. & Inaba, S. (2001). Runaway growth of planetary embryos facilitated by massive bodies in a protoplanetary disk. *Science* 292: 1127-1129.

Kress, M., Brownlee, D. E. & Cody, G. D., III. (2003). What compounds do meteorites contribute to the atmospheres of habitable planets? *NASA Astrobiology Institute General Meeting*: 80 (abstr.).

Kvenvolden, K. A., Lawless, J. G., Pering, K., Peterson, E., Flores, J., Ponnamperuma, C., Kaplan, I. R. & Moore, C. (1970). Evidence for extraterrestrial amino acids and hydrocarbons in the Murchison meteorite. *Nature* 28: 923-926.

Lahav, N. (1999). *Biogenesis: Theories of Life's Origins.* New York: Oxford University Press.

Lahav, M. & Leiserowitz, L. (1999). Spontaneous resolution: From three-dimensional crystals to two-dimensional magic nanoclusters. *Angewault Chemie International Edition* 38: 2533-2535.

Lahav, N., White, D. & Chang, S. (1978). Peptide formation in the prebiotic era: Thermal condensation of glycine in fluctuating clay environments. *Science* 201: 67-69.

Langer, W. D., van Dishoeck, E. F., Bergin, E. A., Blake, G. A., Tielens, A. G. G. M., Velusamy, T. & Whittet, D. C. B.. (2000). Chemical evolution of protostellar matter. In: V. Mannings, A. P. Boss, & S. S. Russell (Eds.). *Protostars and Planets IV* (pp. 29-57). Tucson: University of Arizona Press.

Larralde, R., Robertson, M. P. & Miller, S. L. (1995). Rates of decomposition of ribose and other sugars: Implications for chemical evolution. *Proceedings of the National Academy of Sciences* 92: 8158-8160.

Lawless, J. G. & Yuen, G. U. (1979). Quantitation of monocarboxylic acids in the Murchison carbonaceous meteorite. *Nature* 282: 396-398.

Leshin, L. A. (2000). Insights into Martian water reservoirs from analyses of the Martian meteorite QUE94201. *Geophysical Research Letters* 27: 2017-2020.

Li, K., Chen, R., Zhao, B., Liu, M., Karu, A. E., Roberts, V. A. & Li, Q. X. (1999). Monoclonal antibody-based ELISAs for part-per-billion determination of polycyclic aromatic hydrocarbons; effects of haptens and formats on sensitivity and specificity. *Analytical Chemistry* 71: 302-309.

Lilley, M. D., Butterfield, D. A., Lupton, J. E., Macko, S. A. & McDuff. R. E., (1993). Anomalous CH_4 and NH_4^+ concentrations at a mid-ocean hydrothermal system: Combined effects of sediments and phase separation. *Nature* 364: 45-47.

Lindahl, P. A., Münck, E. & Ragsdale, S. W. (1990). CO dehydrogenase from Clostridium thermoaceticum. *Journal of Biological Chemistry* 265: 3873-3879.

Lippmann, D. Z. & Dix, J. (1999). Possible mechanisms for spontaneous production of enantiomeric excess. In G. Pályi, C. Zucchi & L. Caglioti (Eds.). *Advances in Biochirality* (pp. 85-98). New York: Elsevier.

Liu, R. & Orgel, L. E. (1998). Polymerization of the rocks: α-amino acids and arginine. *Origins of Life and Evolution of the Biosphere* 28: 245-257.

Lovley, D. R. & Phillips, E. J. P. (1988). Novel model of microbial energy metabolism: Organic carbon oxidation coupled to dissimilatory reduction of iron and manganese. *Applied and Environmental Microbiology* 54: 1472-1480.

Luisi, P. L. (1996). Self-reproduction of micelles and vesicles: Models for the mechanisms of life from the perspective of compartmented chemistry. *Advances in Chemistry and Physics* 92: 425-438.

Madigan, M. T., Takigiku, R., Lee, R. G., Gest, H. & Hayes, J. M. (1989). Carbon isotope fractionation by thermophilic phototrophic sulfur bacteria: Evidence for autotrophic growth in natural populations. *Applied Environmental Microbiology* 55: 639-44.

Malin, M. C. & Edgett, K. S. (2000). Evidence for recent groundwater seepage and surface runoff on Mars. *Science* 288: 2330-2335.

Mancinelli, R. L. (1998). Prospects for the evolution of life on Mars, Viking 20 years later. *Advances in Space Research* 22: 471-477.

Mason, S. F. (2000). Extraterrestrial handedness revisited. *Origins of Life and Evolution of the Biosphere* 30: 435-437.

Maule, J., Steele, A., Toporski, J. & McKay, D. S. (2003). A new antibody for category 1 biomarker detection. *Lunar and Planetary Science* XXXIV: #2131 (abstr.).

Mautner, M. N., Conner, A. J., Killham, K. & Deamer, D. W. (1997). Biological potential of extraterrestrial materials. *Icarus* 129: 245-253.

Mazzola, L. T., Frank, C. W., Fodor, S. P., Mosher, C., Lartius, R. & Henderson, E. (1999). Discrimination of DNA hybridization using chemical force microscopy. *Biophysical Journal* 76: 2922-2933.

McCollum, T. M. & Shock. E. L. (1997). Geochemical constraints on chemolithoautotrophic metabolism by microorganisms in seafloor hydrothermal environments. *Geochimica et Cosmochimica Acta* 61: 4375-4391.

McCollom, T. M., Ritter, G. & Simoneit, B. R. T. (1999). Lipid synthesis under hydrothermal conditions by Fischer-Tropsch-type reactions. *Origins of Life and Evolution of the Biosphere* 29:153-166.

McFadden, C. F., Cremer, P. S. & Gellman, A. J. (1996). Adsorption of chiral alcohols on "chiral" metal surfaces. *Langmuir* 12: 2483-2487.

McGovern, P. J., Solomon, S. C., Smith, D. E., Zuber, M. T., Simons, M., Wieczorek, M. A., Phillips, R. J., Neumann, G. A., Aharonson, O. & Head, J. W. (2002). Localized gravity/topography admittance and correlation spectra on Mars: Implications for regional and global evolution. *Journal of Geophysical Research* 107: 10.1029/2001JE001854.

McKay, D. S., Gibson, E. K., Thomas-Keprta, K., Vali, H., Romanek, C., Clemett S., Chillier, X. D. F., Maechling, C. R. & Zare, R. N. (1996). Search for past life on Mars: Possible relic biogenic activity in Martian meteorite ALH84001. *Science* 273: 924-930.

McSween, H. Y., Jr. & Treiman, A. H. (1998). Martian meteorites. In: J. J. Papike (Ed.). *Planetary Materials* (pp. 6-01-6-53). Washington D.C.: Mineralogical Society of America.

Mehta, M. P., Butterfield, D. A. & Baross, J. A. (2003). Phylogenetic diversity of nitrogenase (*nifH*) genes in deep sea and hydrothermal vent environments of the Juan de Fuca Ridge. *Applied and Environmental Microbiology* 69: 960-970.

Messenger, S. (2000). Identification of molecular cloud material in interplanetary dust particles. *Nature* 404: 968-971.

Messenger, S. & Walker, R. M. (1997). Evidence for molecular cloud material in meteorites and interplanetary dust. In: T. Bernatowicz and E. Zinner (Eds.). *Astrophysical implications of the laboratory study of presolar materials*. Woodbury, N.Y.: American Institute of Physics.

Messenger, S., Keller, L. P. & Walker, R. M. (2002). Discovery of abundant interstellar silicates in cluster IDPs. *Lunar and Planetary Science* XXXIII: #1887 (abstr.).

Miller, S. L. (1953). Production of amino acids under possible primitive Earth conditions. *Science* 117: 528-529.

Miller, S. L. & Lazcano A. (1995). The origin of life-did it occur at high temperatures? *Journal of Molecular Evolution* 41: 689-692.

Miller, S. L. & Urey, H. C. (1959). Organic compound synthesis on the primitive Earth. *Science* 130: 245-251.

Mojzsis, S. J., Arrheinius, G., McKeegan, K. D., Harrison, T. M., Nutman, A. P. & Friend, R. L. (1996). Evidence for life on Earth before 3.800 million years ago. *Nature* 384: 55-59.

Mojzsis, S. J., Harrison, T. M. & Pidgeon, R. T. (2001). Oxygen-isotope evidence from ancient zircons for liquid water at the Earth's surface 4,300 Myr. ago. *Nature* 409: 178-181.

Monnard, P.-A. & Deamer, D. W. (2001). Loading of DMPC based liposomes with nucleotide triphosphates by passive diffusion: A plausible model for nutrient uptake by the protocell. *Origins of Life and Evolution of the Biosphere* 31: 147-155.

Monnard, P.-A., Apel, C. L., Kanavarioti, A. & Deamer, D. W. (2002). Influence of ionic solutes on self-assembly and polymerization processes related to early forms of life: Implications for a prebiotic aqueous medium. *Astrobiology* 2: 139-152.

Mukhopadhyay, S., Nittler L. R. & Messenger S. (2002). Hydrogen, carbon and nitrogen isotopic imaging of cluster IDPs. *Meteoritics and Planetary Science* 37 (suppl.): A104 (abstr.).

Mukund, S. & Adams. M. W. W. (1995). Glyceraldehyde-3-phosphate ferredoxin oxidoreductase, a novel tungsten-containing enzyme with a potential glycolytic role in the hyperthermophilic archaeon *Pyrococcus furiosus*. *Journal of Biological Chemistry* 270: 8389-8392.

Nittler, L. R. & Messenger, S. (1998). Hydrogen and nitrogen isotopic imaging of interplanetary dust. *Lunar and Planetary Science* XXIX: #1380 (abstr.).

Ohkuma, M., Noda, S. & Kudo, T. (1999). Phylogenetic diversity of nitrogen fixation genes in the symbiotic microbial community in the gut of diverse termites. *Applied and Environmental Microbiology* 65:4926-4934.

Ono, S., Rumble, D., Pavlov, A., Karecha, P. & Kasting, J. F. (2002). Large S-33 anomalies in late Archean carbonaceous shales, *Eos Transactions of the American Geophysical Union,* Fall Meeting supplement 83: F229-F230.

Orgel, L. E. (1998). Polymerization of the rocks: Theoretical introduction. *Origins of Life and Evolution of the Biosphere* 28: 227-234.

Pasteris, J. D. & Wopenka B. (2002). Images of the Earth’s earliest fossils? *Nature* 420, 476-477.

Pasteur, L. (1848). Recherches sur les relations qui peuvent exister entre la forme cristalline et la composition chimique, et le sens de la polarisation rotatoire. *Annalles de Chimie et Physique* 24: 442-459.

Pasteur, L. (1851). Nouvelles recherches sur les relations qui peuvent exister entre la forme cristalline, la composition chimique et le phénomène de la polarisation rotatoire. *Annalles de Chimie et Physique* 31: 67-102.

Paula, S., Volkov, A. G., Van Hoek, A. N., Haines, T. H. & Deamer, D. W. (1996). Permeation of protons, potassium ions, and small polar molecules through phospholipid bilayers as a function of membrane thickness. *Biophysics Journal* 70: 339-348.

Paull, C. K., Ussler, W., III & Borowski, W. A. (1994). Sources of biogenic methane to form marine gas-hydrates: In situ production or upward migration? *Annals of the New York Academy of Sciences* 715: 392-409.

Pavlov, A. & Kasting, J. F. (2002). Mass-independent fractionation of sulfur isotopes in Archean sediments: Strong evidence for an anoxic Archean atmosphere. *Astrobiology* 2: 27-41.

Pályi, G., Zucchi, C. & Caglioti, L. (1999). *Advances in Biochirality.* New York: Elsevier.

Pendleton, Y. J. & Chiar, J. E. (1997). The nature and evolution of interstellar organics. In: Y. J. Pendleton & A. G. G. M. Tielens (Eds.). *From Stardust to Planetesimals* (pp. 179-200). San Franscisco: Astonomical Society of the Pacific.

Pendleton, Y. J., Sandford, S. A., Allamandola, L. J., Tielens, A. G. G. M. & Sellgren, K. (1994). Near-infrared absorption spectroscopy of interstellar hydrocarbon grains. *Astrophysical Journal* 437: 683-696.

Peters, K. E. & Moldowan, M. J. (1993). *The Biomarker Guide*. New Jersey: Prentice Hall.

Peretó, J., Velasco, A. M., Becerra, A., & Lazcano A. (1999). Comparative biochemistry of CO_2 fixation and the evolution of autotrophy. *International Journal of Microbiology* 2: 3-10.

Phillips, R. J., Zuber, M. T., Solomon, S. C., Golombek, M. P., Jakosky, B. M., Banerdt, W. B., Smith, D. E., Williams, R. M. E., Hynek, B. M., Aharonson, O. & Hauck, S. A., II (2001). Ancient geodynamics and global-scale hydrology on Mars. *Science* 291: 2587-2591.

Pizzarello, S. & Cronin, J. R. (2000). Non-racemic amino acids in the Murray and Murchison meteorites. *Geochimica et Cosmochimica Acta* 64: 329-339.

Podlech, J. (1999). New insight into the source of biomolecular homochirality: An extraterrestrial origin for molecules of life. *Angewault Chemie International Edition* 38: 477-478.

Popa, R. (1997). A sequential scenario for the origin of biological chirality. *Journal of Molecular Evolution* 44: 121-127.

Prasad, S. S. & Huntress, W. T., Jr. (1980). A model for gas phase chemistry in interstellar clouds. II. Nonequilibrium effects and effects of temperature and activation energies. *Astrophysical Journal* 239: 151-165.

Reyes, D. R., Iossifidis, D., Auroux P. -A. & Manz, A. (2002). Micro total analysis systems. 1. Introduction theory and technology. *Analytical Chemistry* 74: 2623-2636.

Rikken, G. L. J. A. & Raupach, E. (2000). Enantioselective magnetochiral photochemistry. *Nature* 405: 932-935.

Robertson, M. P. & Miller, S. L. (1995). An efficient prebiotic synthesis of cytosine and uracil. *Nature* 375: 772-774.

Romanek, C. S., Perry, E. C., Treiman, A. H., Socki, R. A., Jones, J. H. & Gibson, E. K., Jr. (1998). Oxygen isotopic record of silicate alteration in the Shergotty-Nakhla-Chassigny meteorite Lafayette. *Meteoritics and Planetary Science* 33: 775-784.

Rouhi, A. M. (2002). Chiral roundup. *Chemical & Engineering News* 80: 43-57.

Rushdi, A. I. & Simoneit, B. (2001). Lipid formation by aqueous Fischer-Tropsch type synthesis over a temperature range of 100 to 400° C. *Origins of Life and Evolution of the Biosphere* 31:103-118.

Russell, M. J. & Hall, A. J. (1997). The emergence of life from iron monosulfide bubbles at a submarine hydrothermal redox and pH front. *Journal of the Geological Society of London* 154: 377-402.

Russell, M. J., Daia, D. E. & Hall, A. J. (1998). The emergence of life from FeS bubbles at alkaline hot springs in an acid ocean. In: J. Wiegel and M. W. W. Adams (Eds.). *Thermophiles: The Keys to Molecular Evolution and the Origin of Life?* (pp. 77-126). London: Taylor & Francis.

Russell, M. J., Daniel, R. M. & Hall, A. J. (1993). On the emergence of life via catalytic iron-sulphide membranes. *Terra Nova* 5: 343-347.

Saghatelian, A., Yokobayashi, Y., Soltani, K. & Ghadiri, M. R. (2001). A chiroselective peptide replicator. *Nature* 409: 797-801.

Salam, A. (1991). The role of chirality in the origin of life. *Journal of Molecular Evolution* 33: 105-113.

Savarino, J., Cole-Dai, J., Bekky, S., Romero, A., Jackson, T. & Thiemens, M. H. (2002). Sulfur oxidation chemistry preserved in South Pole snow and ice: The origin of sulfur and oxygen mass-independent fractionations generated in plinian eruptions. *Eos Transactions of the American Geophysical Union*, Fall Meeting supplement 83: F221-F222 (abstr.).

Schena M. (2000). *Microarray Biochip Technology*. Natick: Eaton Publishing.

Schoonen, M. A. & Xu, Y. (2001). Di-nitrogen reduction to ammonia with hydrogen sulfide as a reactant under hydrothermal conditions: Implications for the prebiotic synthesis of C-H-O-N compounds. *Eleventh V. M. Goldschmidt Conference*, Contribution No. 1088: #3204. Houston, Tex.: Lunar and Planetary Science Institute. (abstr.)

Schopf, J. W. (1993). Microfossils of the early Archaean Apex Chert: New evidence of the antiquity of life. *Science* 260: 640-646.

Schopf, J. W., Kudryavtsev, A. B., Agresti, D. G., Wdowiak, T. J. & Czaja, A. D. (2002). Laser-Raman imagery of Earth's earliest fossils. *Nature* 416: 73-76.

Schrenk, M. O., Kelley, D. S., Delaney, J. R., & Baross J. A. (In Press, 2003). Incidence and diversity of microorganisms within the wall of an active deep-sea hydrothermal vent sulfide structure. *Applied and Environmental Microbiology*.

Schultze-Lam, S., Ferris, F. G., Konhauser, K. O. & Wiese, R. G. (1995). *In situ* silicification of an Iceland hot spring microbial mat: Implications for microfossil formation. *Canadian Journal of Earth Sciences* 32: 2021-2026.

Scott, J., Fogel, M., O'Brien, D. & Emerson, D. (2003). Utilizing compound specific isotopes as bio-indicators of prokaryote metabolism. *NASA Astrobiology Institute General Meeting 2003*: 485 (abstr.).

Seager, S. (In Press, 2003). The search for Earth-like extrasolar planets. *Earth and Planetary Science Letters*.

Seager, S. & Sasselov, D. D. (2000). Theoretical transmission spectra during an extrasolar giant planet transit. *Astrophysical Journal* 537: 916-921.

Seager, S., Whitney, B. A. & Sasselov, D. D. (2000). Photometric light curves and polarization of close-in extrasolar giant planets. *Astrophysical Journal* 540: 504-520.

Segré, S., Deamer, D. W. & Lancet, D. (2001). The lipid world. *Origins of Life and Evolution of the Biosphere* 31:119-145.

Shapiro, R. (1988). Prebiotic ribose synthesis: A critical review. *Origins of Life and Evolution of the Biosphere* 18: 71-85.

Shapiro, R. (1995). The prebiotic role of adenine: A critical analysis. *Origins of Life and Evolution of the Biosphere* 25: 83-98.

Sharma, A., Scott, J. H., Cody, G. D., Fogel, M. L., Hazen, R. M., Hemley, R. J. & Huntress, W. T. (2001). Microbial activity at gigapascal pressures. *Science* 295: 1514-1516.

Sherwood Lollar, B., Westgate, T. D., Ward, J. A., Slater, G. F. & Lacrampe-Couloume, G. (2002). Abiogenic formation of alkanes in the Earth's crust as a minor source for global hydrocarbon reservoirs. *Nature* 416: 522-524.

Shew, R. & Deamer, D. W. (1983). A novel method for encapsulating macromolecules in liposomes. *Biochimica et Biophysica Acta* 816: 1-8.

Shimoyama, A., Naraoka, H., Komiya, M. & Harada, K. (1989). Analyses of carboxylic acids and hydrocarbons in Antarctic carbonaceous chondrites, Yamato-74662 and Yamato-793321. *Geochemical Journal* 23: 181-193.

Shock, E. L., McCollum, T. & Schulte, M. D. (1996). Geochemical constraints on chemolithoautotrophic reactions in hydrothermal systems. *Origins of Life and Evolution of the Biosphere* 25: 141-159.

Shu, F., Najita, J., Galli, D., Ostriker, E. & Lizano, S. (1993). The Collapse of clouds and the formation and evolution of stars and disks. In: E. H. Levy & J. I. Lunine (Eds.). *Protostars and Planets III* (pp. 3-45). Tucson: University of Arizona Press.

Silver, V. S. & Postgate, J. R. (1973). Evolution of asymbiotic nitrogen fixation. *Journal of Theoretical Biology* 40:1-10.

Siskin, M., Brons, G., Katritzky, A. R. & Balasubramanian, M. (1990). Aqueous Organic Chemistry. 1. Aquathermolysis: Comparison with Thermolysis in the reactivity of Aliphatic compounds. *Energy & Fuels* 4: 475-492.

Smith, J. V., Arnold, F. P., Jr., Parsons, I. & Lee, M. R. (1998). Biochemical evolution. I. Polymerization on internal, organophilic silica surfaces of dealuminated zeolites and feldspars. *Proceedings of the National Academy of Sciences* 95: 3479-3485.

Smith, J. V., Arnold, F. P., Jr., Parsons, I. & Lee, M. R. (1999). Biochemical evolution. III. Polymerization on silica-rich surfaces, crystal-chemical modeling, formation of first cells, and geological clues. *Proceedings of the National Academy of Sciences* 96: 3479-3485.

Smyth, J. R. & Bish, D. L. (1988). *Crystal Structures and Cation Sites of the Rock-Forming Minerals.* Boston: Allen & Unwin.

Soai, K., Osanai, S., Kadowaki, K., Yonekubo, S., Shibata, T. & Sato, I. (1999). d- and l-quartz-promoted highly enantioselective synthesis of a chiral organic compound. *Journal of the American Chemical Society* 121: 11235-11236.

Sokolava, T. G., González, J., Kostrikina, N. A. Chernyh, N. A., Tourova, T. P., Bonch-Osmolovskaya, E. A. & Robb, F. (2002). Anaerobic CO-oxidizing, H_2-producing prokaryotes from volcanic habitats. In: Astrobiology Expeditions Workshop, March 25-29. St. Petersburg, Russia: Russian Astrobiology Center (abstr.).

Solomon, S. C., Aharonson, A., Banerdt, W. B., Dombard, A. J., Frey, H. V., Golombek, M. P., Hauck, S. A., II, Head, J. W., III, Johnson, C. L., McGovern, P. J., Phillips, R. J., Smith, D. E. & Zuber, M. T. (2003). Why are there so few magnetic anomalies in Martian lowlands and basins? *Lunar and Planetary Science* XXXIV: #1382 (abstr.).

Sowerby, S. J., Edelwirth, M. & Heckl, W. M. (1998a). Self-assembly at the prebiotic solid-liquid interface: Structures of self-assembled monolayers of adenine and guanine bases formed on inorganic surfaces. *Journal of Physical Chemistry B* 102: 5914-5922.

Sowerby, S. J., Edelwirth, M., Reiter, M. & Heckl, W. M. (1998b). Scanning tunneling microscopy image contrast as a function of scan angle in hydrogen-bonded self-assembled monolayers. *Langmuir* 14: 5195-5202.

Sowerby, S. J., Heckl, W. M. & Petersen, G. B. (1996). Chiral symmetry breaking during the self-assembly of monolayers from achiral purine molecules. *Journal of Molecular Evolution* 43: 419-424.

Steele, A. & Toporski, J. (In Press, 2003). Astrobiotechnology. In: *2nd European Exo- and Astrobiology Workshop*. Noordwijk: European Space Agency Publication Division.

Steele, A., Goddard, D. T., Stapleton, D., Toporski, J. K. W., Peters, V., Bassinger, V., Sharples G., Wynn-Williams, D. D. & McKay, D. S. (2000). Imaging of an unknown organism on the Martian meteorite ALH84001. *Meteoritics and Planetary Science* 35: 237-241.

Stinson, S. C. (2001). Chiral chemistry. *Chemical & Engineering News* 79: 45-56.

Stroud, R. M., O'Grady, M., Nittler, L. R. & Alexander, C. M. O'D. (2002). Transmission electron microscopy of an in situ presolar silicon carbide grain. *Lunar and Planetary Science* XXXIII: #1785 (abstr.).

Summons, R. E. & Walter, M. R (1990). Molecular fossils and microfossils of prokaryotes and protests from Proterozoic sediments. *American Journal of Science* 290: 212-244.

Summit, M. & Baross. J. A. (1999). Thermophilic subseafloor microorganisms from the 1996 North Gorda Ridge eruption. *Deep-Sea Research II* 45: 2751-2766.

Swindle, T. D., Treiman, A. H., Lindstrom, D. J., Burkland, M. K., Cohen, B. A., Grier, J. A., Li, B. & Olson E. K. (2000). Noble gases in iddingsite from the Lafayette meteorite; evidence for liquid water on Mars in the last few hundred million years. *Meteoritics and Planetary Science* 35: 107-115.

Thomas-Keprta, K. L., Clemett, S. J., Bazylinski, D. A., Kirschvink, J. L., McKay, D. S., Wentworth, S. J., Vali, H., Gibson, E. K., Jr., McKay, M. F. & Romanek, C. S. (2001). Truncated hexa-octahedral magnetite crystals in ALH84001: Presumptive biosignatures. *Proceedings of the National Academy of Sciences* 98: 2164-2169.

Tivey, M. K. (1995). The influence of hydrothermal fluid composition and advection rates on black smoker chimney mineralogy: Insights from modeling transport and reaction. *Geochimica et Cosmochimica Acta* 59: 1933-1949.

Toporski, J., Steele, A., Westall, F., Avci, R., Martill, M. & McKay, D. S. (2002a). Morphological and spectral investigation of exceptionally well preserved bacterial biofilms from the Oligocene Enspel formation, Germany. *Geochimica et Cosmochimica Acta* 66: 1773-1791.

Toporski, J., Steele, A., Westall, F., Thomas-Keprta, K. & McKay, D. S. (2002b). The simulated silicification of bacteria - new clues to the modes and timing of bacterial preservation and implications for the search for extraterrestrial microfossils. *Astrobiology* 2: 1-26.

Treiman, A. H. (1993). Preterrestrial aqueous alteration of the Lafayette (SNC) meteorite. *Meteoritics and Planetary Science* 28: 86-97.

Tsuchida, R., Kobayashi, M. & Nakamura, A. (1935). Asymmetric adsorption of complex salts on quartz. *Journal of the Chemical Society of Japan* 56: 1339.

Tuck, A. (2002). The role of atmospheric aerosols in the origin of life. *Surveys in Geophysics* 23: 379-409.

Twidale, M., Randall, D. & Bentley, R. (1994). Situated evaluation for cooperative systems. In: R. Furuta & C. Neuwirth (Eds.). *CSCW '94: Transcending Boundaries: Proceedings of the Conference on Computer Supported Cooperative Work* (pp. 441-452). New York: Association for Computing Machinery.

Uchihashi, T., Okada, T., Sugawara, Y., Yokoyama, K. & Morita, S. (1999). Self-assembled monolayer of adenine base on graphite studied by noncontact atomic force microscopy. *Physical Review B* 60: 8309-8313.

Vali, H., McKee, M. D., Ciftcioglu, N., Seras, S. K., Plows, F. L., Chevet, E., Ghiabi, P., Plavsic, M., Kajander, E. O. & Zare, R. N. (2001). Nanoform: A new type of protein-associated mineralisation. *Geochimica et Cosmochimica Acta* 65: 63-74.

van Zuilen, M., Lepland, A. & Arrhenius, G. (2002). Reassessing the evidence for the earliest traces of life. *Nature* 418: 627-630.

Wächertshäuser, G. (1988). Before enzymes and templates: Theory of surface metabolism. *Microbiological Reviews* 52: 452-484.

Wächtershäuser, G. (1992). Groundworks for an evolutionary biochemistry: The iron-sulphur world. *Progress in Biophysics and Molecular Biology* 58: 85-201.

Wainwright, N. R. & Child, A. (1999). Use of amplified microbial detection assays in life detection and planetary protection studies. *Workshop on Mars 1999.* (# 2554). Houston: Lunar and Planetary Institute. (abstr.)

Walde, P., Wick, R., Fresta, M., Mangone, A. & Luisi, P. L. (1994). Autopoietic self-reproduction of fatty acid vesicles. *Journal of the American Chemical Society* 116: 11649-11654.

Ward, B. B. & Priscu, J. C. (1997). Detection and characterisation of denitrifying bacteria from a permanently ice-covered Antarctic lake. *Hydrobiologia* 347: 57–68.

Wasserman, S. & Faust, K. (1994). *Social Network Analysis*. Cambridge, Mass.: Cambridge University Press.

Weber, A. L. (1998). Prebiotic amino acid thioester synthesis: Thiol-dependent amino acid synthesis from formose substrates (formaldehyde and glycolaldehyde) and ammonia. *Origins of Life and Evolution of the Biosphere* 28: 259-270.

Weber, A. L. (2001). The sugar model: Catalysis by amines and amino acid products. *Origins of Life and Evolution of the Biosphere* 31: 71-86.

Weinberger, A. J., Becklin, E. E., Schneider, G., Chiang, E. I., Lowrance, P. J., Silverstone, M., Zuckerman, B., Hines, D. C., & Smith, B. A. (2002). Infrared views of the TW Hydra disk. *Astrophysical Journal* 566: 409-418.

Weinberger, A. J., Becklin, E. E., Schneider, G., Smith, B. A., Lowrance, P. J., Silverstone, M. D., Zuckerman, B. & Terrile, R. J. (1999). The circumstellar disk of HD 141569 imaged with NICMOS. *Astrophysical Journal* 525: L53-L56.

Weinberger, A. J., Becklin, E. E., & Zuckerman, B. (2003). The first spatially resolved mid-infrared spectroscopy of Beta Pictoris. *Astrophysical Journal* 584: L33-L37.

Wellman, B. (1988). Structural analysis: From method and metaphor to theory and substance. In: B. Wellman & S. D. Berkowitz (Eds.). *Social Structures: A Network Approach* (pp. 19-61). Cambridge: Cambridge University Press.

Westall, F. (1998). The oldest fossil mineral bacteria from the Early Archaean of South Africa and Australia. In: J. Chela-Flores and F. Raulin (Eds.). *Exobiology: Matter, Energy, and Information in the Origin and Evolution of Life in the Universe* (pp.181-186). Amsterdam: Kluwer Academic Publishers.

Westall, F., de Wit, M. J., Dann, J., van der Gaast, S., de Ronde, C. E. J. & Gerneke, D. (2001). Early Archaean fossil bacteria and biofilms in hydrothermally-influenced, shallow water sediments, Barberton greenstone belt, South Africa. *Precambrian Research* 106: 93-116.

Wetherill, G. W. (1994a). Possible consequences of absence of “Jupiters’’ in planetary systems. *Astrophysics and Space Science* 212: 23-32.

Wetherill, G. W. (1994b). Provenance of the terrestrial planets. *Geochimica et Cosmochimica Acta* 58: 4513-4520.

Wetherill, G. W. (1996). The formation and habitability of extra-solar planets. *Icarus* 119: 219-238.

Wilde, S. A., Valley, J. W., Peck, W. H. & Graham, C. M. (2001). Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr. ago. *Nature* 409: 175-178.

Yakovleva, J., Davidsson, R., Lobanova, A., Bengtsson, M., Eremin, S., Laurell, T. & Emnèus, J. (2002). Microfluidic enzyme immunoassay using silicon microchip with immobilized antibodies and chemiluminescence detection. *Analytical Chemistry* 74: 2994-3000.

Zehr, J. P. & Capone, D. G. (1996). Problems and promises of assaying the genetic potential of nitrogen fixation in the marine environment. *Microbial Ecology* 32: 263-281.

7. Plan for Strengthening the Astrobiology Community

7.1 Education and Public Outreach

Background

The Carnegie Institution of Washington (CIW) has been working since 1989 to improve science, mathematics, and technology education for students nationally and locally in the Washington, D.C., public schools. The Carnegie Institution of Washington's Education and Public Outreach (E/PO) programs are dedicated to the increase and diffusion of knowledge among children, teachers, and the general public about the natural world. To accomplish this goal, the institution develops, presents, and promotes educational programs and materials so that science can be understood, valued, and enjoyed.

The E/PO plan for the CIW NAI team blends new and traditional approaches to bring teachers, children, and the general public relevant astrobiology-related content and experiences. Just as the institution's astrobiology efforts engage the science community in highly focused research, so the E/PO program engages the public in a highly-leveraged learning adventure that elevates the understanding of the nature of science. The broad and deeply connected field of astrobiology presents unusually clear opportunities not only to teach about the science but also about the nature of science itself, an important dimension of the National Science Education Standards.

Accomplishments to Date

Over the past five years, the Carnegie Institution has involved educators and scientists to produce a variety of unique materials and experiences for elementary students and teachers. Highlights of our E/PO accomplishments include the following:

1. Involved all lead scientists in astrobiology-related E/PO activities that last year reached 8,000 teachers, students, and members of the general public.

2. Produced and distributed 10,000 copies of the booklet *Astrobiology: The Search for Water.*

3. Developed significant collaborations with outside partners, such as the Smithsonian Institution, to produce over 75 book/activity backpacks for Pre-K-2 students that developmentally explored some of the fundamental ideas related to astrobiology. The packs are being used in a pilot program in over 25 schools in the District of Columbia. Backpack topics included Water, Life on Earth, Small Life, Past Life, and Fossils.

4. Trained over 300 District of Columbia teachers as part of the five-week Carnegie Academy for Science Education (CASE) Summer Science Institute. For three years, CASE has used astrobiology as a way to organize thematically instruction and content. CASE programs require the active involvement of lead scientists.

5. Produced and distributed over 22,000 copies of a poster and associated educational materials entitled *Astrobiology: Discovering New Worlds of Life*. This poster and an accompanying article were published in the November-December 2001 issue of *Science Scope*, the journal of the National Science Teachers Association (NSTA).

6. Collaborated with NAI on the creation of activities for a series of educational posters for grades K-12.

7. Collaborated with NAI partners (JSC and JPL) on the production of a comprehensive set of astrobiology materials for the elementary level entitled *Ice in the Solar System*.

8. Featured the science of astrobiology in over a dozen Capital Science Lectures, each attended by an average of 200 local high-school students and interested citizens of the District.

E/PO Goals for the Next Five Years

We propose several new projects that over the course of the coming five years will sustain contact with millions of youngsters, teachers, and the general public in order to promote concepts and ideas related to astrobiology. Over the next five years the Carnegie Institution's E/PO effort, under the leadership of Julie Edmonds, will:

1. Involve all lead scientists in direct participation in the institution's E/PO efforts;

2. Place special emphasis on reaching local underserved urban communities;

3. Place strong emphasis on K-8 education, including educational technology components, educator workshops, and curriculum support activities;

4. Place strong emphasis on informal science learning through participation of museums and libraries;

5. Leverage partnerships such as TIME For Kids, NSTA, Smithsonian Institution, NOVA (WGBH-TV), Platypus Media, and others, in order to reach a national audience;

6. Team with the Minority Institution Astrobiology Collaborative on E/PO projects.

TIME For Kids (No-cost leverage)

Six years ago, Time Magazine, Inc., initiated a new division called *TIME For Kids*. *TIME For Kids* (TFK) is a weekly news publication for youngsters that presents a context for science, history, art, and culture. The publication reaches over 4 million children through classroom subscriptions and another 200,000 through *Time* magazine subscriptions.

TIME For Kids is already well known in America's classrooms as the nation's fastest growing educational news magazine, but TFK is much more than a magazine. Whether experienced online, in print, or through a vast array of educational products and resources, TFK delivers a vital tool for teachers and a unique avenue for K-6 students to connect with the world around them and feel empowered to play a role in it. The voice of TFK features the expertise of educators, scientists, publishers, veteran journalists, content experts, as well as one of the premier cadres of young reporters in the country.

Science forms a significant core of content for *TIME For Kids*. Over the course of the next five years, CIW and *TIME For Kids* will begin a partnership to promote astrobiology through content, feature articles, interactive web components, and teacher resources. CIW will support *TIME For Kids* in the following ways:

1. Access to scientists for interviews by *TIME For Kids* young reporters.

2. Press releases, content summaries, and activity outlines related to new and cutting-edge research in the field of astrobiology.

3. Supplementary print and visual materials published by CIW, NASA, and NAI that will enhance both the print and web medium.

Carnegie Frontiers – a Collaborative Effort to Create a Children's Book About Microbes

As part of CIW's E/PO efforts, a series of publications entitled *Carnegie Frontiers* was created to highlight the institution's related research in various aspects of the field of astrobiology. Over the course of five years, three publications were created and distributed to teachers across the country through NSTA, direct mail, and regional distribution by cooperating museums and institutions. The titles were *Astrobiology: The Search for Water* (a 15-page booklet), *Astrobiology: New Worlds of Life* (a poster was featured in the NSTA publication *Science Scope* along with an article about astrobiology), and *Astrobiology: Ice in the Solar System*, an instructive CD with accompanying activities information and visuals about ice in our Solar System. (This CD is now in production).

Plans for the next five years include two new additions to the *Carnegie Frontiers* series. The first new release in the series will emerge from collaboration between CIW, other NAI members, and a private publishing house that specializes in science-related books for youngsters. The collaborative will create and publish a 64 page, full-color children's book about the microbial world with over 70 original illustrations and high-quality photographs. This trade book about microbes will introduce children (8-12 years of age) to the science of astrobiology through a connected and engaging story line of scientific content about life and the natural world. The resulting book with accompanying teacher's guide will be distributed to libraries, schools, NAI partners, and bookstores nationwide.

Carnegie Academy for Science Education (No-cost leverage)

The Carnegie Academy for Science Education (CASE) was established in 1993 as a professional development program for pre-Kindergarten through 6th-grade public school teachers in Washington, D.C. The program's mission is to train teachers to align instruction with national science and math standards and integrate interactive activities, assessment, and content into their classroom curriculum.

Over the last three years a centerpiece of CASE has been the DC ACTS initiative, a collaborative project based on the premise that systemic reform of science, mathematics, and technology education can support positive changes for all parts of the educational system. The Carnegie Institution of Washington, the American Association for the Advancement of Science (AAAS), and the District of Columbia Public School system are collaborators on this project. CASE provides the elementary-school component. The middle-school and high-school teacher training is the responsibility of the AAAS. Other CASE programs include the following:

- *Summer Science Institute.* The only long-term professional development program in science for District of Columbia Public School teachers.

- *Yearlong series of six-week courses.* These yearlong sessions train some 200 additional teachers in District schools. As with the Summer Institutes, teachers receive graduate credits upon completion of the courses.

- *Mentor Teachers.* Outstanding CASE teachers are selected each year to receive additional training and return the following summer as members of the teaching staff of the Science and Mathematics Institutes.

- *Model Schools.* CASE helps 15 D.C. public elementary schools develop coherent, standards-based, pre-K to 6th-grade science and mathematics programs. Model Schools receive additional curriculum materials and workshops. Citywide expansion of this component of the program is planned for September 2004.

• *First Light*. Since 1989, First Light continues as a free Saturday science school and also serves as a "laboratory" for testing CASE's instructional methodologies. The free, 5-hour classes attract some 30 neighborhood children on a first-come, first-served basis every school year. In addition to participating in hands-on science activities, students go on weekly field trips and receive free lunches.

CASE participants, young and old, develop their scientific sensibilities through the incorporation of topics such as astrobiology that serve as points of connection for understanding biology, astronomy, geology, and chemistry. Astrobiology themes are embedded during the CASE Summer Science Institutes, monthly trainings, and workshops. Thematic topics of instruction include microbial life, extremophiles, hydrothermal vent morphology, evolution of life on Earth, NASA mission design, planetary geology, and the discovery of extrasolar planets. Classroom activities, readings and regular instructional dialogues by staff scientists combine to create a professional development experience for teachers that is vibrant and provides the necessary content and instructional models for classroom use.

Smithsonian Institution Display

The Smithsonian Institution's National Museum of Natural History (NMNH) is host to nearly 7 million visitors annually. As part of this proposal's E/PO effort, NMNH and CIW will jointly oversee the production of a display in the Constitution Avenue lobby that will focus visitors' attention on the science of astrobiology. The display will allow for printed material for the public as well as a display of artifacts and images. Such an exhibit will feature the joint research of the Smithsonian and the Carnegie Institution, as well as the NAI overall.

The Minority Institution Astrobiology Collaborative

The Minority Institution Astrobiology Collaborative (MIAC) is a national initiative, based at Tennessee State University, that aims to advance the cause of education and research in astrobiology among minority communities in the United States. The goals of MIAC are to bring together participating members and other organizations to share expertise and resources in order to create an environment for faculty and students of minority institutions in which significant contributions to the field of astrobiology in education and research are made; to provide support and professional development for college and university faculty and K-12 teachers to teach astrobiology content; and to collaborate with NAI lead teams and in 5-to-10 years to become a NASA Astrobiology lead team. MIAC will assist CIW in the implementation of the following of its E/PO efforts.

1. Minority faculty and student research opportunities;

1. Student internships;

2. CASE instructional support;

3. Development of the trade book for children on microbes;

4. Professional development opportunities for Pre-K-12 teachers.

Summary of Astrobiology-related Education and Public Outreach Activities by the Carnegie Institution of Washington

Activity	Product	Description	Budget	Lead organization(s)
2003-2004 Development of trade book for children on microbes	Nationally distributed trade book	The proposed project would be the creation of a 64-page, full color children's book about the microbial world with over 70 original illustrations and high-quality photographs. This trade book will introduce children (8-12 years of age) to the science of astrobiology through connected and engaging scientific content about microbes, life, and the natural world.	Year 1. $45,000 Year 2. $45,000	CIW, NAI partners, Platypus Media
2003-2008 *TIME For Kids* articles and content	Articles, interviews and web-features as part of a nationally distributed periodical.	Science forms a significant core of content for the publication *TIME For Kids*. Over the course of the next 5 years, CIW and *TIME For Kids* will begin a partnership to promote astrobiology through content, feature articles, interactive web components, and teacher resources.	No cost	CIW, *TIME For Kids*, NAI members
2003-2008 CASE instructional support	Professional development for teachers, workshops, instructional support, and materials for classrooms.	The DC ACTS initiative is a collaborative professional-development project based on the premise that systemic reform of science, mathematics, and technology education can support positive changes for all parts of the educational system. The Carnegie Institution of Washington, the American Association for the Advancement of Science, and the District of Columbia Public School system are collaborators on this project. CASE provides the support and training for the elementary school component.	No cost - funded by CIW, NSF, HHMI	CIW, AAAS, DCPS
2003-2008 Capital Science Lectures	Series of public lectures	Free public talks designed to help non-scientists understand scientific thinking and to appreciate the importance of basic research in our lives today. Each year, a selection of speakers has been chosen to focus on the institution's interest in astrobiology.	No cost - funded by CIW and other partners	CIW, NAI partners
2003-2008 Website	Website	Maintain CIW astrobiology website with E/PO components that include activities, a section for students and teachers, as well as content and a calendar of activities.	No cost - funded by CIW	CIW
2006-2008 Informal science learning	Museum exhibits	A dedicated astrobiology-related display in the Constitution Ave. lobby of the Smithsonian Natural History Museum	Year 3. $16,000 Year 4. $7,000	Smithsonian NAI partners
2003-2008 Involvement of minority institutions	Minority Institution Astrobiology Collaborative	The involvement of MIAC in the following E/PO efforts: 1. Minority faculty and student research opportunities 2. Student internships 3. CASE instructional support 4. Development of trade book for children on microbes 5. Professional development of Pre-K-12 teachers	Year 1. $4,000 Year 2-5. $3,000/year	MIAC and CIW

7.2 Professional Community

Members of the Carnegie Institution NAI team have played a large role in helping the field of astrobiology develop, through their service on advisory groups, review panels, conference organizing committees, and other efforts that strengthen the professional astrobiology community. We provide here a selection among the activities that CIW NAI Co-Is have undertaken in support of astrobiology during the last five years, activities of the type that we intend to continue to pursue over the coming five years as well.

Advisory Groups. Co-Is have served on the NASA Astrobiology Roadmap team (Boss, Deamer), the NRC Committee on the Origin and Evolution of Life (Baross as Co-chair and Deamer and Fogel as members), the NASA Solar System Exploration Subcommittee (Solomon), the NASA Astronomical Search for Origins Subcommittee (Weinberger), the NRC Task Group on Sample Return from Small Solar System Bodies (Baross), the NRC Steering Committee on Size Limits of Very Small Microorganisms (Baross), the NASA Space Science Advisory Committee (Deamer), the Mars Exploration Payload Assessment Group (Baross, Farquhar), the NASA Terrestrial Planet Finder Science Working Group (Seager), and the NASA Navigator Program Independent Review Team (Boss). Solomon chaired and Deamer served on a Review Panel for NASA Specialized Centers of Research and Training (NSCORTs) in Astrobiology.

Editorial Positions. Boss serves as Series Co-Editor for the Cambridge University Press *Astrobiology Series* and is on the scientific advisory board for the book *Meteorites and the Early Solar System II*; Baross, Deamer, Fogel, Hazen, Solomon, and Steele serve on the Editorial Board for the journal *Astrobiology*, and Baross serves as a Co-Editor for the Springer-Verlag Press *Advances in Astrobiology and Biogeophysics Series* and for *Planets and Life: The Emerging Science of Astrobiology*.

NAI Focus Groups. Members of the Carnegie Institution NAI team have been active on NAI Focus Groups, including the current focus groups on Mars (Alexander, Hauri, Solomon), Mission to Early Earth (Ono, Solomon), Europa (Solomon), Astromaterials (Alexander, Nittler), and Titan (Baross, Hazen). Seager is chairing an effort that will culminate in a formal proposal for an Astronomy Focus Group (to also include Boss, Butler, and Weinberger), and Steele is leading an effort that will result in a proposal for a Biotechnology Focus Group.

Hosting Laboratory Visits. The Carnegie Institution has hosted laboratory visits by more than 30 astrobiologists from other institutions, including six NAI teams, two NAI foreign associate or affiliate organizations, one of the two NSCORTs in Astrobiology, and half a dozen other institutions in the U.S. and abroad.

Scientific Conference Organization. The Carnegie Institution hosted the Second NAI General Meeting in 2001, and team members served on the scientific organizing committees (SOCs) for that meeting (Boss, chair), the Second Astrobiology Science Conference in 2002 (Baross, Boss), and the Third NAI General Meeting in 2003 (Baross, Brandes). The Carnegie Institution also hosted the Conference on Scientific Frontiers in Research on Extrasolar Planets in 2002 (Seager served as SOC chair and Boss was a SOC member) and a workshop on Water on Mars in 2002 (Co-chairs Alexander and Boctor). Boss chaired the Gordon Research Conference on Origins of Solar Systems in 1999, and this year's conference features four team members as speakers and discussion leaders (Alexander, Desch, Seager, Weinberger). Cody is the vice-chair of this year's Gordon Conference on the Origin of Life, and he will chair the conference on that topic in 2005. Baross co-chaired the NRC Workshop on Life Detection in 2000 and chaired the University of Washington Origin of Life Conference in 2001. Boss serves on the SOCs for the Bioastronomy 2004 conference and the Protostars and Planets V Conference in 2005.

Departmental Seminar Series. Both DTM and the GL host a weekly seminar series. A large fraction of those seminars, typically attended by scientists from throughout the Washington, D.C., area, focus on astrobiological topics. In addition, NAI team members at the Carnegie Institution participate via teleconference in a weekly Astrobiology Journal Club hosted by the NSCORT in Astrobiology at the Rensselaer Polytechnic Institution.

International Organizations. Boss chairs and Butler serves on the International Astronomical Union Working Group on Extrasolar Planets. Deamer serves as Second Vice President for the International Society for the Study of the Origin of Life and is the Editor of their online newsletter.

7. 3 Training

The CIW-led NAI team has been actively engaged in training the next generation of astrobiologists through collaboration with neighboring universities, through research training of competitively selected undergraduate and high-school students, and through the recruitment and training of predoctoral and postdoctoral scientists. We plan to continue these efforts throughout the next 5 years of participation in NAI.

Teaming with Neighboring Universities

Although CIW is not a degree-granting institution, there is strong interest among universities in the region to develop instructional programs in astrobiology, and discussions have been initiated regarding the involvement of CIW staff in teaching programs at those universities.

In the spring of 2002 the Virginia State Council for Higher Education approved a new Ph.D. degree track in Astrobiology as part of the Biosciences Department at George Mason University. This degree program was developed in close collaboration among scientists at George Mason University, NASA, the Carnegie Institution, and the American Type Culture Collection. Several members of the CIW NAI team, including Co-Investigators Emerson, Hazen, and Huntress, will teach courses as part of this program. During the 2002-03 academic year Hazen developed and taught the first new offering in this program – a 2-semester graduate seminar entitled “The Literature of Astrobiology.” The first student to enroll in this Ph.D. program, Ms. Mary Ewell, will begin her thesis research at the Carnegie Institution during the summer of 2003.

At the four university partners on this NAI team, the Co-Investigators from those institutions are committed to the involvement of students in their astrobiological research within NAI. Budget requests from those four institutions all include funds for student support.

Carnegie Institution Summer Intern Program

Beginning in 1997 the Carnegie Institution initiated a dynamic summer research program for high-school and undergraduate student interns. During the 10-week summer program, sponsored in part by the NSF Research Experiences for Undergraduates Program and the Camille and Henry Dreyfus Foundation, each student works on his or her own research project with one or more of scientific staff at the Broad Branch Road Campus (encompassing the Department of Terrestrial Magnetism and the Geophysical Laboratory). Ninety-one students have participated during the past six summers; they were mentored by a total of 54 Carnegie scientists. This nationally advertised program has proven especially successful in attracting women and minority students; last year's group of 20 interns, for example, included 12 women and 3 minority students. For the past three years the Director of the summer intern program has been Dr. William Minarik. Additional information on this program may be found on our web site: http://www.gl.ciw.edu/interns/.

In addition to working on their own research projects, the interns meet as a group at least weekly for an informal lunch with one or more of our scientific staff. During these lunches the staff share their own experiences of "becoming a scientist" with the students, describe their present research interests with a tour of their labs, and answer questions about scientific careers. A group of predoctoral and postdoctoral fellows also meet with the interns for lunch, during which the main topic of discussion centers on graduate school selection and job opportunities. The interns are given tours to local scientific organizations, for example the Gem, Mineral and Meteorite Collection at the Smithsonian Institution, and laboratories at the United States Geological Survey and the NASA Goddard Space Flight Center. The interns also spent one afternoon participating in Carnegie's CASE Summer Science Institute, the science teacher education program also sponsored by the NSF (see above). Another component of the intern program is a biweekly afternoon scientific ethics seminar on topics such as treatment of coworkers, laboratory misconduct, whistle blowing, and co-authorship.

Each intern’s primary effort centers on a research project that is supervised by one or more Carnegie staff scientists. The character of the student-mentor interaction ranges from scenarios in which a student works closely with his or her mentor every day, to instances in which the students receive input from senior personnel once or twice a week. The nature of these interactions also changes with time: At the beginning of the program the students are very dependent on their advisors for guidance, but as the program progresses most acquire sufficient laboratory skills to work more independently. At three points during the program, as interns prepare research proposals, abstracts, and final research papers, advisors are required to review their student’s written work and discuss their progress. The program director also monitors student progress and is available throughout the summer to address any concerns the students or advisors might have on a daily basis. At the end of the summer the students present the results of their work at a symposium attended by their advisors as well as by other staff.

On the basis of the experience of students from the last six summers, the intern program opens doors for other scientific opportunities. Several of the students have presented their work at national scientific meetings, several have coauthored papers on the research carried out during their internship, and a few have won recognition for their work. Lora Armstrong (2000) and Jean Li (2001) were a semi-finalist and finalist, respectively, in the Intel Science Talent Search, and last year intern Kevin Gan won a $50,000 scholarship from the Siemens Westinghouse Competition in Math, Science, and Technology. Nearly all of the students in our program expressed an interest during their internship in applying to graduate school in the sciences, and many are now pursing graduate degrees at top universities.

Participation in the NAI has provided exciting opportunities for our summer interns, expanding both the number of student applicants and the breadth of their experience. Training of interns in topics related to astrobiology — notably planetary formation, high-pressure methods, and organic chemistry — has played, and will continue to play, an important role in our team’s mission within NAI. During the 2002 summer intern program 7 of the 20 interns pursued research topics of astrobiological interest, ranging from circumstellar disks and organic materials in meteorites to prebiotic chemical reactions and the preservation of biomarkers in fossil materials. To continue to involve interns in astrobiological research projects, we seek a modest contribution to the continuation of the summer intern program from NAI.

Predoctoral and Postdoctoral Fellow Programs

For more than half a century the Carnegie Institution has sponsored an internationally recognized program for predoctoral and postdoctoral fellows. A hallmark of these training programs at the Carnegie Institution’s Broad Branch Road Campus is the close collaborative ties among staff scientists with backgrounds in astronomy, biology, chemistry, geology, and physics.

All fellows (as well as summer research interns) are encouraged to participate in the full range of campus activities, including seminars, workshops, group meetings, and collaborative research.

The Broad Branch Road campus of the Carnegie Institution currently supports approximately 15 predoctoral and 50 postdoctoral fellows (typically two- or three-year positions) annually. All positions are advertised internationally, and candidates are subject to a rigorous selection process. Prospective candidates are required to submit a research proposal and supporting documents. Most candidates who pass a first screening are invited to present a campus seminar prior to selection.

For each of the past five years, six Carnegie postdoctoral fellows have been engaged in research in some area of astrobiology and have been supported half time by NAI, with the remainder of their support provided by Carnegie Institution funds. We propose to raise that number to 7 postdoctoral fellows per year in years 2 and 3 of this project and 8 per year in years 4 and 5, with the same stipulation that each of these individuals would be supported in equal measure by NAI and the Carnegie Institution. NAI fellows are encouraged to spend a portion of their time at one or more of the partner institutions of our team or at an institution of one of the other NAI teams, and each will be expected to attend at least one NAI or related conference each year.

During the past five years, 17 individuals have been supported as NAI Fellows at the Carnegie Institution. While some of these individuals are still at a postdoctoral stage in their career, others have gone on to academic and research positions where they have initiated astrobiological research programs of their own. Three are Co-Investigators on this proposal. Those individuals, and their current positions, are

Jay Brandes	Assistant Professor, University of Texas (Co-I, this proposal)
Joakim Bebie	Now pursuing a career in art
Kenneth Chick	Research Staff, Dynamics Technology, Inc.
Steven Desch	Carnegie NAI Fellow
Andrew Dombard	Research Staff, Washington University
Timothy Filley	Assistant Professor, Purdue University
Nader Haghighipour	Carnegie NAI Fellow
Karl Kehm	Assistant Professor, Washington College
Michelle Minitti	NAI/NRC Postdoctoral Fellow, Arizona State University
Sujoy Mukhopadhyay	Carnegie NAI Fellow (will accept an Assistant Professor position at Harvard University this fall)
Larry Nittler	Staff Member, Carnegie Institution (Co-I, this proposal)
Eugenio Rivera	Carnegie NAI Fellow
Anurag Sharma	Carnegie NAI Fellow
James Scott	Staff Member, Carnegie Institution (Co-I, this proposal)
Sarah Stewart-Mukhopadhyay	Carnegie NAI Fellow (will accept an Assistant Professor position at Harvard University this fall)
Jan Toporski	Carnegie NAI Fellow
Susan Ziegler	Assistant Professor, University of Arkansas

We regard it as noteworthy as well that in the first three years of the NAI/National Research Council Postdoctoral Fellowship program, two of the 18 individuals awarded fellowships to date (Henry Scott and Michael Smoliar) have chosen to accept their fellowship at the Carnegie Institution. A third fellow (Michelle Minitti) was a Carnegie Fellow (supported half time by NAI) at the time of her selection, and a fourth (Kevin Boyce) is collaborating with members of the Carnegie NAI team in the course of his postdoctoral research.

7.4 Teaming with Minority Institutions

The Carnegie Institution is committed to expanding the involvement of individuals from underrepresented minorities in the science of astrobiology, from students at all levels of education to active scientific professionals. As described in **Section 7.1**, CIW is partnering with the Minority Institution Astrobiology Collaborative (MIAC) at Tennessee State University on research opportunities for minority faculty and students, on providing internships for minority students, on providing instructional support from the Carnegie Academy for Science Education for schools in underserved neighborhoods, and on providing development opportunities for Pre-K-12 teachers in such schools. MIAC will also serve as a partner with CIW on the development of a trade book on microbes for children that will feature astrobiological themes.

CIW was also one of three NAI institutions that hosted a participant in the NAI Minority Institution Faculty Sabbatical Program last year. Through that program, Prof. M. F. Mahmood from Howard University spent the summer of 2002 in the laboratory of Co-Investigator Andrew Steele. Prof. Mahmood, an expert on optical devices, worked on the application of advanced laser and microfluidic concepts for bioassays on Mars. The collaboration has been a fruitful one; Prof. Mahmood has continued his visits on a weekly basis since the summer, and he and Steele have identified several follow-on projects of mutual interest. A proposal naming Prof. Mahmood as a collaborator has been written, and discussions have been initiated on inviting Howard University graduate students to carry out a portion of their Ph.D. research working at the Carnegie Institution under the supervision of NAI Co-Investigators.

7.5 Staff

In the first five years of its membership in NAI, the Carnegie Institution has made a major commitment to astrobiological research through its appointment of new members of the Research Staff. On the same day that the initial selection of the first NAI teams was made, Wesley Huntress agreed to join the Carnegie Institution as Director of the Geophysical Laboratory (GL). In his previous position as the NASA Associate Administrator for Space Science, Huntress had fostered both the discipline of astrobiology and the creation of NAI. As GL Director one of his early goals was strengthening the department's staff in microbiological aspects of astrobiology. As a result, Andrew Steele and James Scott were recruited to the staff in 2001 and 2002, respectively.

At the Carnegie Institution's Department of Terrestrial Magnetism, the last four additions to the Research Staff are all now Co-Investigators on our NAI team. These include astronomers Paul Butler (who joined DTM in 1999), Alycia Weinberger (2001), and Sara Seager (2002), and cosmochemist Larry Nittler (2001).

The Carnegie Institution's Postdoctoral Fellow program constitutes a less direct contribution to staffing in astrobiology. In particular, a number of the individuals who have carried out research in astrobiology while at the Carnegie Institution now have permanent faculty or research positions where they are continuing to make scientific contributions to the field (**Section 7.3**). Carnegie staff members and Co-Investigators Nittler and Scott were formerly Postdoctoral Fellows supported in part by NAI. Two other graduates of the institution's postdoctoral program, Jay Brandes and James Farquhar, now have university faculty positions and are Co-Investigators on this proposal.

7.6 Facilities

The institutional partners of this consortium collectively offer an extraordinarily rich diversity of laboratories, analytical capabilities, and other facilities to the NASA Astrobiology

Institute. All of these facilities are currently in operation, and all will be open to the full membership of NAI.

Carnegie Institution of Washington

At the Carnegie Institution's Geophysical Laboratory, there are several well-equipped laboratories that will be utilized in support of NAI research. A Stable Isotope Laboratory has the capability to provide high-precision, high-accuracy stable isotopic analyses of a broad range of materials including gases, solutions, and solids and inorganic and organic materials. We support a Thermo-Finnigan MAT 252 Isotope Ratio Mass Spectrometer (IRMS) dedicated to the analysis of the three isotopes of oxygen; and a Finnegan Delta plus Excel IRMS with a variety of interfaces, including an elemental analyzer (EA), a thermal conductivity elemental analyzer (TCEA), and a gas chromatograph (GC). This instrument is capable of providing stable isotopic data for hydrogen, carbon, nitrogen, oxygen, and sulfur in both organic and inorganic solids. The fully automated EA and TCEA interfaces provide fast throughput analysis of bulk samples, the GC provides for compound specific analysis. We recently installed a new Thermo-Finnigan MAT 253 IRMS dedicated to simultaneous analysis of the four isotopes of sulfur (in the form of SF_6 derivatives). Our laboratory can accommodate both in-line and off-line fluorination chemistry, necessary to measure three isotope fractionations in the oxygen and sulfur systems. Toward this end we support a UV excimer laser — Lambda-Physik for use with KrF (248 nm) and ArF (193nm) fill gases — for *in situ* "spot" analysis and multiple CO_2 IR lasers for analysis of mineral chips and powders.

A Molecular Organic Analysis Laboratory is equipped with a broad range of analytical instrumentation for the analysis of complex organic materials. For the analysis of soluble organic compounds seven gas chromatographs are available with different injector and detector options. For example, we have two quadrupole mass spectrometer detectors with both electron impact (EI) and chemical ionization (CI) sources. Other detectors include nitrogen-phosphorus detectors, sulfur-selective electron-capture detectors, and numerous flame ionization detectors (FIDs) and thermal conductivity detectors (TCDs). Available injectors include standard split/splitless and temperature-programmable. We also have two pyroprobe interfaces for pyrolysis GC and GC-MS studies. For the analysis of non-derivatized or less volatile samples we have an HPLC with both UV-visible and fluorescence detection.

For the analysis of organic solids the laboratory is equipped with a three-channel solid-state nuclear magnet resonance (NMR) spectrometer (Varian-Chemagnetics CMX Infinity 300) bundled with three double resonance probes, ^{1}H and ^{19}F and X (^{15}N-^{31}P) maximum Magic Angle Spinning (MAS) speeds of 7, 12, and 30 kHz, respectively; one triple-resonance probe ^{1}H or ^{19}F and X + Y (^{15}N-^{31}P) with a maximum spinning speed of 18 kHz, and one single-resonance combined rotation and multipulse spectroscopy (CRAMPS) probe for ^{1}H or ^{19}F. Supporting these probes our NMR has one narrow-band high-power RF amplifier (^{1}H or ^{19}F) and two broad-band high-power RF amplifiers.

For the measurement of vibrational and optical properties of organic molecules and biological matter at high pressures, a custom-built laser micro-optical system for precise work in diamond anvil cells permits high-pressure Raman spectroscopic studies. This system contains Spectra Physics 165 and 171 ion lasers, a Spex 1877 spectrograph, a Dilor XY spectrograph, and a small spectrometer for blackbody and ruby fluorescence measurements (for pressure determination). We also have both a Fourier Transform Infra Red (FTIR) spectrometer as well as an FTIR microscope.

The Molecular Biology Laboratory includes a Surface Enhanced Laser Desorption Ionization-Time of Flight (SELDI-ToF) mass spectrometer (Ciphergen protein chip reader); a Genepix microarray reader, for both nucleic acid and protein arrays; and an Agilent bioanalyzer, with DNA, RNA, and protein electrophoresis and flow cytometry. Also available are an Olympus BX61 fluorescence microscope with SIS image analysis software; PCR and real-time PCR; denaturing gradient gel electrophoresis (DGGE) and temperature gradient gel electrophoresis (TGGE); ELISA; single nuecleotide polymorphisms (SNP); and ATP luminometry analytical instrumentation. A portable PCR machine is available for field studies. Finally we also have stereo, biological, atomic force, and hand-held digital microscopes to support microbiological research.

The Carnegie Institution's Department of Terrestrial Magnetism (DTM) has several state-of-the-art instruments for trace element and high-precision isotope analysis. The DTM Cameca 6f ion microprobe is equipped with both oxygen and cesium primary ion sources and an electron flood gun for charge compensation. The 6f offers significant improvements in such areas as primary ion beam current densities, secondary ion transmission, and computer automation over earlier models. Among other applications for tasks described in this proposal, the ion microprobe will be used for *in situ* analysis of alteration features in meteorites to understand the conditions during alteration and the origin of the fluids. We are also developing a second high-transmission, multi-collector (5 faradays/multipliers) secondary beamline for the 6f using a large magnet from an accelerator mass spectrometer. It will have capabilities that are similar to or better than the Cameca 1270 ion microprobe. We expect to obtain our first data from the new beamline by June 2003.

A JEOL 6500F thermal field-emission scanning electron microscope (SEM) has been recently installed at CIW. This instrument allows secondary and backscatter electron imaging with a routine spatial resolution of better than 5 nm. Elemental mapping can be performed with a 0.5-•m spatial resolution using an energy-dispersive and a wavelength-dispersive spectrometer (EDS and WDS, respectively). The WDS is optimized for light elements providing a >10-fold increase in C count rates over EDS. Also, an electron backscatter diffraction camera and associated software allows crystallographic information to be obtained in the SEM.

DTM has two inductively-coupled plasma (ICP) mass spectrometers, a VG P54 and a VG Axiom. Both are used for high-precision isotopic analysis. The Axiom is now equipped with a multiple faraday/multiplier detector array, enabling analysis of samples with very large variations in isotopic abundances. The fast switching capability of the Axiom magnet means it can also be used for major/trace element analysis. However, we have recently acquired a VG PQ2 ICP that will be used exclusively for trace element analysis. We also have a CETAC LSX-200 UV laser-ablation system for *in situ* microanalyses of trace elements and isotopes. The department operates two thermal-ionization mass spectrometers for radiogenic isotope analysis. Also available are labs for mineral separation, as well as binocular and petrographic microscopes with digital image acquisition and processing.

The computing environment at DTM includes a wide range of workstations. The theoretical calculations of the DTM astronomy group are enabled by the Carnegie Alpha Cluster, a cluster of over 40 Alpha chip processors running Red Hat Linux. This cluster, supported in large part by the NSF, provides Co-I Boss and others with supercomputer-class computer power at a small fraction of the cost. A second cluster of 16 Intel Xeon 2.2 GHz machines is used to support orbital dynamics calculations. Two high-speed, broadband T1 lines to nearby NASA Goddard Space Flight Center connect the local DTM and GL Ethernet to the Internet.

The astrometric search for Solar System analogues by Co-Investigators Boss and Weinberger will utilize the Carnegie Institution's Las Campanas Observatory, located at an elevation of 7,200 feet in the Chilean Andes. NSF support and Carnegie matching funds have been requested in order to build a new astrometric camera for use at the Cassegrain focus of the DuPont 2.5-m telescope. With the new camera, the group expects to be able to achieve astrometric accuracies of 0.25 milliarcseconds, sufficient for the detection with a signal-to-noise ratio of 4 of a Jupiter-analogue planet orbiting a solar-mass star 5 parsecs distant from the Sun.

American Type Culture Collection, George Mason University

The American Type Culture Collection (ATCC) is a private not-for-profit institution founded by scientists in 1925 to serve as a national repository and distribution center for cultures of microorganisms. Although the ATCC now takes on special contracts through its Applied Sciences Group and offers a variety of workshops, the principal business of the ATCC remains the acquisition, maintenance, and distribution of microorganisms and related biological materials in support of the scientific community's needs. The ATCC is on 26 acres adjacent to the George Mason University Prince William Campus. The custom-designed, 104,000 ft^2 headquarters building houses the administration, state-of-the-art microbiology laboratories, and an operations area. The operations area, where the actual collection resides, has a media preparation area and a preservation lab for lyophilization and programmed freezing of cultures. The culture repository provides 8,200 ft^2 of storage area, including a 2,500-ft^2 cold room for storage at 4°C, 55 ultra-low mechanical freezers (-70°C), and space for 65 vapor-phase liquid-nitrogen freezers (-170°C). All freezers are equipped with dual, independent temperature monitoring and recording systems. Both systems trigger facility alarms that are monitored on-site continuously and are backed by third-party, central station monitoring.

Co-Investigator David Emerson's 800-ft^2 laboratory is well-equipped for routine microbiological work, including centrifuges, biosafety cabinets, and incubators. He has complete facilities for doing anaerobic microbiology, including a COY anaerobic glove box. He also has an Olympus BX-60 epifluoresence microscope equipped with an Optronics CCD camera for low-light imaging. Other equipment in his lab includes an Applikon 3-l bioreactor, a gas chromatograph, a Bio-Rad Biologic HPLC system, a PCR machine, a gell electrophoresis apparatus and gel documentation systems, -80°C freezers and a liquid-N_2 storage tank, centrifuges, a walk-in cold room, a UV/visible spectrophotometer, peristaltic pumps and other equipment for development of microcosm studies, a French press, and a variety of incubators. In addition Emerson's lab has a variety of workstations with software that includes the complete Bionumerics suite, S-Plus, MacVector, and the GCG package.

State-of-the-art facilities exist on site for doing molecular biology and genomics. These include two ABI 377 DNA sequencers, multiple PCR machines, Diversilab lab-on-a-chip genotyping system using rep-PCR, Micromass-Waters MALDI-TOF-MS, a MIDI FAME system, a Biolog system for phenotypic characterization of bacteria, and a Qualicon Riboprinting system for genotyping of bacteria.

Naval Research Laboratory

The Naval Research Laboratory (NRL) has extensive facilities for electron microscopy studies, including two 300-kV conventional transmission electron microscopes (TEMs) and one 200-kV field-emission transmission electron microscope, a field emission scanning electron microscope, and a focused ion beam (FIB) instrument, as well the standard array of sample preparation tools, e.g., argon ion mill, dimpler, and metallurgical microscopes. The field-emission TEM is a high-resolution analytical instrument, with atomic-resolution Z-contrast imaging, sub-nanometer probe size for energy dispersive X-ray spectroscopy, and energy loss spectroscopy. It should remain an important facility for the analysis of returned samples over the next decade. Co-Investigator Stroud is in charge of the operation of this microscope. The FEI200 FIB at the NRL will be available for preparing thin membrane sections of interstellar dust particles, meteorites, and fossilized materials for *in situ* and *ex situ* characterization, as well as for extracting grains from ion or electron probe mounts after automated analysis. A new dual-beam FIB, scheduled for purchase by NRL in 2004, will improve the speed and quality with which these sections can be prepared.

Smithsonian Institution

The combined facilities of the Smithsonian Institution's Laboratories of Analytical Biology encompass approximately 20,000 ft^2 in three Washington, D.C., locations: The genetics laboratory of the National Zoological Park, a large molecular biology and biochemistry facility in Suitland, Maryland, and a small multipurpose laboratory plus an SEM facility on the mall in the Natural History Building (NHB). As part of the NAI, the facilities unique to the Smithsonian at Suitland and the NHB will be available to NAI members on a cost-recovery basis. The facilities and equipment include complete pre-PCR facilities (separate from the PCR facilities) for sample extraction with all necessary grinding and extraction devices, centrifuges, 8-ft laminar flow hood, incubators, shakers and low-temperature storage. A fully-equipped PCR facility includes two MJ Research Tetrads, a Robocycler, multiple Perkin Elmer PCR units, an Opticon real-time PCR unit, multiple centrifuges, gel rigs, and an Eagle Eye unit for visualization. There is also a fully equipped dedicated cloning area containing a DNA sequencing service on an ABI 3100 for both fragment and sequence determination, sequencing analysis software, and multiple phylogenetic software packages.

A recently acquired state-of-the-art ToF SIMS IV has been installed in the Department of Mineral Sciences. It is equipped with a high-spatial-resolution (> 100 nm) liquid Ga ion source and a dual-source sputter column (Cs^+, Ar^+, and O_2^+). ToF-SIMS is capable of virtually simultaneous collection of all secondary ions of a given polarity, which allows us to image major, minor, and many trace element species in a specimen. Additionally, molecular species up to 10,000 AMU can be detected, allowing for localization of organic compounds on unprepared surfaces. Operated in a dual-ion mode, a sample can be imaged in 2D in one pass and then the surface sputtered in another. This allows for shallow depth profiling (100s of nm) and the creation of 3D secondary ion images of inorganic substrates.

A new full-spectrum imaging Energy Dispersive Spectrometer (EDS) system (Thermonoram Vantage 3) has been mounted on a conventional tungsten-source Scanning Electron Microscope (JEOL 840A). The solid-state detector processes X-ray pulses digitally, allowing for high-speed collection. Moreover, X-rays of all energies are collected at each electron beam position during mapping, which enables one to reconstruct energy spectra.

A LaB_6 FEI XL30 Environmental Scanning Electron Microscope (ESEM) located in the Laboratory for Analytical Biology is available to examine specimens in their native state (uncoated). Even fully hydrated samples can be imaged as the water pressures ranging up to 20 torr can be achieved. The instrument is equipped with several high-pressure gaseous secondary electron (GSE) detectors, a large area GSE for low-magnification imaging, as well as a solid-state backscattered electron detector.

An Electron Probe MicroAnalyzer *(*EPMA) is a five-wavelength spectrometer microprobe with a sixth integrated solid-state detector (JEOL 8900R). It is used routinely for quantitative analyses, stage X-ray imaging of large areas, and offline data reduction, and it has been kept under service contract since its installation 6 years ago. A cathodoluminescence (CL) microscope and spectrometer consists of a high-sensitivity true-color CCD camera (Optronics MagnaFire) mounted on a beam-regulated benchtop luminoscope (SpectruMedix ELM-3R). Light spectra (UV-VIS-NIR) are collected with a solid-state detector (Santa Barbara Group ST) and a McPherson 272 monachrometer. A new set of high-transmission long-working-distance lens have recently improved the luninoscope optics and allow for higher magnifications, which benefits both the imaging of fine CL features and the spectra collection.

The institution maintains several controlled-atmosphere experimental facilities, including two Deltech one-atmosphere, gas-mixing ($CO-CO_2$) furnaces with oxygen sensors for precise measurement of oxygen fugacity and programmable temperature controllers with maximum operating temperatures of ~1650°C. There is a vacuum oven for storage of starting materials.

The Smithsonian holds the National Collections of Meteorites, Rocks & Ores, and Minerals, all of which are invaluable resources for the study of prebiotic chemistry and mineral-microbe interactions. Co-Investigator McCoy is Curator-in-Charge of the Meteorite Collection.

University of California, Santa Cruz

Co-I Deamer's laboratory will make use of, and make available to other NAI investigators, a $50,000 Zeiss digital microscope to perform microscopic examination of self-assembled molecular systems and to record images. Additional instrumentation includes matrix assisted laser desorption ionization (MALDI)-ToF and electrospray mass spectrometry to analyze samples. Co-I Deamer plans to continue his collaboration with Richard Zare at Stanford University, whose laser-desorption laser-ionization mass spectrometer (L^2MS) instrument will be used to identify PAHs in Kamchatka samples.

University of Maryland

Laboratory facilities at the University of Maryland include wet chemical and gas-source mass spectrometry capabilities for analysis of $\delta^{17}O$, $\delta^{18}O$, $\delta^{33}S$, $\delta^{34}S$, and $\delta^{36}S$. A Finnigan MAT Delta Plus mass spectrometer with continuous-flow and dual inlet capabilities was installed in October 2001, and a four collector, oil-free Finnigan MAT 253 with continuous-flow and dual inlet capabilities was installed in June 2002. The Finnigan MAT 253 is used for high-precision measurements of $\Delta^{33}S$ and $\Delta^{36}S$.

The laboratory also has an Excimer Compex 110 UV laser and New Wave beam delivery system and two IR CO_2 lasers with home-made beam delivery systems. These lasers are used for fluorination of sulfur and oxygen compounds for isotopic analysis and also as light sources for photochemical experiments. In addition to the laser fluorination capabilities, there are extraction manifolds for on-line pyrolysis of oxygen-bearing compounds and on-line fluorination of silver sulfide. There is a 10-bomb reaction manifold that will allow for rapid throughput of silver sulfide samples that are difficult to handle with laser fluorination techniques. Experience with bomb fluorinations of silver sulfide and a Finnigan MAT 252 at UCSD indicates that accuracy and precision of $\Delta^{33}S$ and $\Delta^{36}S$ can be significantly better than +/- 0.02 and 0.3 per mil, respectively. The present system yields uncertainties significantly better than this (0.007 and 0.10 per mil, respectively).

Wet chemical facilities have been built for extraction and analysis of sulfur in trace sulfate, organic sulfur compounds, elemental sulfur, monosulfide, and disseminated pyrite. Facilities for oxygen analysis will include a focus on analysis of oxygen in salts, silicates, oxides, and organic compounds. The availability of these techniques will allow for a variety of analytical questions to be addressed that are different from the *in situ* and mineral separate work that is presently being undertaken at CIW.

The laboratory has a high-power deuterium lamp and grating monochrometer for photochemical experiments chosen specifically because it radiates at different wavelengths than the high-pressure mercury arc lamp at GL, and it could be used for complementary experiments. We have a solar UV chamber that would be available for other experiments that require UV. Maryland also houses two additional gas-source mass spectrometers (directed by J. Kaufman), two magnetic-sector ICP instruments with UV laser ablation capabilities at 213 nm and 293 nm (directed by R. Ash and W. McDonough), two thermal-ionization mass spectrometers, clean-lab facilities (directed by R. Walker and P. Tomascak), and a JEOL EPMA (directed by P. Piccoli).

University of Texas

The University of Texas Marine Science Institute has a variety of instruments and facilities available for the proposed NAI study. Major instrumentation includes a ThermoFinnigan Delta Plus Isotope Ratio mass spectrometer coupled to a Carlo Erba NC2500 elemental analyzer sample-preparation unit available for analysis of up to 100 samples per day for C and N isotopic values. An additional compound-specific interface consisting of a TRACE GC, ThermoFinnigan MAT Precon unit, and GC PAL Autosampler provides the capability to analyze compounds from gasses (N_2, CH_4, CO_2, N_2O) to high-molecular-weight hydrocarbons, fatty acids, and amino acids (with derivitization). In addition a Waters/Hewlett-Packard gradient HPLC with UV/visible and fluorescent detectors is available for analyses of amino acids, amines, fatty acids, and other compounds.

University of Washington

Located in the Oceanography Research Building, three laboratories totaling approximately 1200 ft^2 of space are equipped with fume hoods, Milli-Q water, gas and air, and most of the standard equipment for culturing anaerobic hyperthermophiles and for routine biochemical and molecular biological work. One of the laboratories is a designated high-temperature, high-pressure facility. Shared equipment available in the School of Oceanography includes four cold rooms, three autoclaves, sonicators, lyophilizers, coulter counters, and a dark room. There is also a dedicated molecular biology laboratory in the College of Ocean and Fisheries Sciences equipped with DNA sequencers, PCR equipment, and a Pharmacia FPLC system for protein purification, and the university has facilities for electron microscopy, peptide synthesis, and protein microsequencing.

Major items of equipment available include a Packard Tri-carb 4000 scintillation counter, a Sorvall RC5C high-speed centrifuge, a Zeiss UEM photomicroscope equipped with epifluorencence capabilities, a Perkin Elmer UV/VIS LAMBDA 25 spectrometer equipped with a Peltier Temperature Programmer (PTP-6), a Forma Scientific anaerobic hood with a built-in anaerobic high-temperature incubator, five high-temperature oil baths, four constant high-temperature air incubators, a Varian 3400 gas chromatograph, an IBM LC/9533 HPLC, a Packard Picolite Luminometer for measuring bio- and chemi-luminescence, a Amicon RA2000 ultrafiltration system, three Eppendorf microcentrifuges, electrophoretic equipment, a PCR system, and an ultracold freezer. The pressure laboratory is equipped with 30 stainless-steel pressure vessels designed for use to 200°C and 0.2 GPa, a computer-controlled high-temperature/high-pressure incubator, and a rocking high-temperature/high-pressure incubator designed for subsampling during incubation without loss of pressure and temperature and for continuous culture studies.

Advanced Light Source

The Scanning Transmission X-ray Microscope (STXM) resides at beamline 5.3.2 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. The instrument is dedicated to the analysis of organic polymers by X-ray Absorption Near Edge Spectro (XANES)-microscopy at the K edges of carbon, nitrogen, and oxygen. A bending magnet is used to provide a sufficiently brilliant X-ray beam (1×10^6 photons/second at the sample) in energy range spanning the range 150 to 600 eV. The nominal resolving power is 3000 across this energy range with the use of a spherical grating monochromator. X-ray focusing is achieved with a Fresnel-zone plate objective providing a 40-nm spot size.

7.7 Flight Missions

A number of the investigators on this proposal are involved in spacecraft missions, including flight missions, missions under development, and missions now in the planning stages.

PI Solomon is a member of the Mars Orbiting Laser Altimeter Team on the Mars Global Surveyor mission and is the Principal Investigator for the MESSENGER (MErcury Surface, Space ENvironment, GEochemistry, and Ranging) mission. The MESSENGER spacecraft, selected for flight under NASA's Discovery Program, is scheduled to launch in 2004 and will fly by Venus and Mercury twice each en route to one year of orbital observations at Mercury in 2009-2010.

Co-Is Alexander and Cody are developing two microanalytical techniques, XANES and STXM, for the analysis of organic matter in small samples, including the cometary particles that will be returned by the Stardust mission. Alexander and Co-I Hauri are also involved in the development of a large-radius, high-transmission, multicollector ion microprobe that will be used for the analysis of samples to be returned by the Stardust and Genesis missions.

Co-I Boss is on the Science Team for NASA's Kepler mission, scheduled for launch in 2007. Kepler's photometric observations will permit the detection of numerous Earth-like planets in Earth-like orbits around stars in the disk of our galaxy, offering the first estimate of the frequency of Earth-like planets. Boss is also a member of the Navigator Program Independent Review Team (NP IRT), which reports to NASA Headquarters and has oversight responsibility for all elements of the Navigator Program, including the Keck Interferometer, the Large Binocular Telescope Interferometer, the Space Interferometry Mission, and the Terrestrial Planet Finder (TPF). During 2003, Boss will chair a sub-committee of the NP IRT that will be charged with reviewing the Science Plan for the TPF mission.

Co-I Deamer has proposed, in collaboration with scientists at NASA Ames Research Center, the development of a particle detector and analyzer for a future Mars polar lander.

Co-I Farquhar has been involved in first-phase analytical development and testing of protocols for analysis of oxygen isotopes in diamond as a member of the Genesis Science Team.

Co-I Huntress is presently involved in a concept study for the Comet Sample Return mission under NASA's New Frontiers Program, and he is leading a proposal to NASA's Discovery Program for a Venus Orbiter and Probe mission.

Co-I McCoy is a collaborator on the Gamma Ray Spectrometer team on the Mars Odyssey mission, and he serves on a team preparing a proposal to NASA's Discovery Program for a mission to return a sample from 433 Eros. McCoy is also part of a science team for a neutron generator gamma-ray spectrometer designed for astrobiological prospecting. The instrument, currently under consideration for support by NASA's Astrobiology Science and Technology Instrument Development (ASTID) Program, is intended for the solicitation for the next rover mission to Mars.

The Carnegie Institution has recently purchased, with funding from NASA's Sample Return Laboratory Instrument and Data Analysis Program, a field-emission scanning electron microscope that will be used by Co-Is Nittler and Alexander to examine cometary and interstellar dust returned by the Stardust mission. Nittler and Alexander are also collaborating with Kenneth Grabowski at the Naval Research Laboratory to improve an accelerator mass spectrometer there to enable high-sensitivity elemental analyses of solar-wind particles returned by the Genesis mission.

Co-I Seager is a Co-Investigator for the Legacy Program and the Galactic Plane Survey on the Space Infrared Telescope Facility (SIRTF). The SIRTF mission is scheduled to launch in April. Seager is also a member of the Terrestrial Planet Finder Scientific Working Group and serves as a Support Scientist for the Microvariability and Oscillations of Stars (MOST) Microsatellite, to be launched by the Canadian Space Agency in June.

Co-I Steele serves as science team leader on a space flight concept to use biosensors to detect life, microbial contamination, and organic materials on Mars. Initially entitled Mars Immunoassay Life Detection Instrument (MILDI) and funded by NASA under the 2005 fundamental biology AO, the instrument concept has been renamed Modular Assays for Solar System Exploration (MASSE). This instrument utilizes technology currently available in laboratories to extract liquid samples, processes these samples, and inoculates both enzyme- and microarray-based detection systems. Positive reactions are monitored by a change in fluorescence. Current microarray technology allows the interrogation of up to 6 million probes in a space the size of a normal glass slide. Originally developed for the human genome project, this technology is being modified with minimal engineering to contain antibodies to a range of terrestrial compounds that indicate viable and fossil life, contamination, and prebiotic organic material and may be further tailored to look for exotic chemistries indicative of non-Earth-centric life. The instrument concept has been developed to a demonstration stage by collaborators in Spain, and Steele's group is currently designing a breadboard version containing a micro-fluidic sample handling system. The work is being carried out in collaboration with Johnson Space Center, Jet Propulsion Laboratory, Lockheed Martin, Montana State University, and the Centro de Astrobiología.

7.8 Information Technology

Background. A successful virtual institute needs not only technical expertise but also a clear understanding of how technology must be implemented to support the institution. By necessity NAI requires broad-band internet and state-of-the-art technology to access a wide range of distributed environments, including both traditional units where non-traditional work environments have been implemented and those that exist across organizational boundaries — such as distributed scientific teams, ad hoc project teams or focus groups of limited duration, and a super-group of inter-organizational teams and institutes. Virtual team members therefore can work across space, or organizational boundaries, or both. The needs of a true virtual institute can be met only with non-traditional work-environments, such as telecommuting, satellite work centers, and telemetry. These obvious goals notwithstanding, the history of information systems is laden with many expensive technological failures, mainly attributable to ignorance of social and scientific knowledge about the groups, organizations, and behavioral systems for which they were to be used. Currently CIW scientists participate actively in the virtual collaboration projects led by the Collaborative Research Support Group at NAI Central. These projects include the NAI member Needs Assessment Survey, the Collaborative Tools Comparison Study pilots, and NAI video seminar series. The IT point of contact for the CIW NAI team, Gotthard Sághi-Szabó, is an active member of the NAI IT Working Group, which meets periodically via videoconference to discuss issues associated with the development of the virtual institute. Sághi-Szabó has attended face-to-face IT meetings during a 5-day NAI IT conference held at Ames Research Center in April 2002, and he presented a "live" poster at the 2003 NAI General Meeting. The poster introduced the CIW astrobiology website (http://astrobiology.ciw.edu/), a collaborative and educational tool developed in-house by the CIW IT group. This group has also participated in the development of a website and collaboration tool for the Modular Assays for Solar System Exploration (MASSE) project and designed and built an online survey tool to support the decision-making process of the Mars Exploration Program Analysis Group (MEPAG) community (http://mepag.gl.ciw.edu/). Last year, the CIW IT group began to introduce social science methodologies to the analysis of social, psychological, and scientific interaction among CIW team elements and team members as a model for the future development of the NAI virtual institute.

Proposed Work. As part of our proposed work, we will develop a comprehensive conceptual framework that has the necessary embedded constructs and variables to define properly teams and organizations, including virtual entities. This framework will be deployed for the study of the CIW astrobiology team and NAI overall as working examples of highly diverse virtual groups. The first question we seek to address is whether NAI and the virtual teams were correctly set up with traditional organizational practices in mind. In other words, does the current approach meet good management and organizational effectiveness criteria? As an integral part of the NAI institute we plan to study the critical components of a virtual institute, including organizational stability, security of membership, reward and recognition systems, clarity of objectives, directions, project plans, motivation and influence processes, leadership methods, the quality of personnel, team involvement and project visibility, stability of goals and priorities, built-in organizational control systems, conflict management, trust-building methods, decision making, and creative problem-solving processes. We will focus on devising mechanisms to prevent conformity, group-think, and negative organizational politics, all possible attributes of a highly connected virtual institute. We will consider means for increasing entity attractiveness and cohesiveness.

We further propose to analyze specific factors and challenges to virtual entities. The major challenges to virtual team effectiveness originate from the lack of face-to-face interactions, indirect communication, and coordination difficulties. Due to the limited time-span and intrinsic multi-disciplinary, cross-functional, cross-organizational nature of many interactions, virtual organizations may be unable to reach a “critical mass” of communication and information sharing that is fundamental to the group's or organization's success. Therefore, periodic face-to-face meetings are still necessary for teams involved in communication-intensive tasks. Virtual teams might also experience reduced effectiveness due to confusion arising from a lack of social context cues during electronic interaction, the difficulty of enforcing group norms and roles, and ambiguity in the communication process further amplified by physical-temporal distances and socio-cultural-technical differences. Communication and collaboration patterns and methods, trust relations, and managerial methods should be analyzed and optimized if the concept of the virtual institute is to be realized. An ethnographic approach (Twidale et al. 1994), wherein the behavior and attitudes of the team members can be observed in the context of their work, will be used to gather information during meetings and the scientific collaboration process. Electronic data and information exchange will be collected and analyzed using the Social Network Analysis approach (Wasserman & Faust 1994; Haythornthwaite 1996; Wellman 1988). This latter method focuses on patterns of relations among people and organizations and will provide us with invaluable results regarding the extent and effectiveness of our virtual entities. The overall measure of an entity's performance will be defined by the innovative ideas produced, goals accomplished, project outcomes achieved, adaptability to change, personnel and team commitment, and stakeholders' satisfaction.

Because of the limited time-span of virtual entities, and their multi-disciplinary, cross-functional, cross-organizational nature, traditional system design life cycles may be too slow to help groups to reach a “critical mass” of communication and information sharing. Time is obviously a critical factor for IT support. In order to accelerate the information system lifecycle process, we propose to investigate the feasibility of implementing modern system development and deployment methods, including disruptive technologies, prototyping, joint application design, nominal group techniques, rapid application deployment, and group support systems.

Information on the technological requirements associated with the varied activities of the virtual entities will be collected. We propose to test tools and methodologies that will best suit the needs of intra-, and inter-group communications, managerial, control, and administrative functions, decision-support functions, scientific collaboration, problem solving, and knowledge management processes. The NAI Collaborative Research Support Group has identified several technical challenges, including hardware and software incompatibilities, differences in available network bandwidth, uneven access to collaboration tools, issues regarding ease of use, uneven local IT support, and differences in individual learning curves among participating scientists regarding this new technology. NAI Central has identified the most desired electronic tools by current NAI members, e.g., internet presentations and real-time meeting tools, desktop videoconferencing tools, document- and data-sharing tools, and knowledge management tools. This assessment clarified current NAI member user requirements with regard to available technology. Particularly important objectives recognized during this assessment include cross-platform compatibility, ease of use, desktop accessibility of tools, web-based access, high speed, reliability, security, and low cost.

CIW's IT team proposes to follow the important groundwork laid by NAI Central with a proactive strategy to try to match the growth in demand for software and hardware that can be used to manage and coordinate scientific projects, people, and activities. Apart from traditional information system support tools, such as websites, mailing lists, instant messaging, video conferencing, and teleconferencing, we are testing and developing collaborative *Knowledge Base*, *Incident-reporting* or *Issue-tracking*, *Bug Tracking*, *Resource & Asset Management*, and *Project Management* systems. Distance remains the principal barrier to managers and scientists in the virtual world. Carefully chosen information and communication technologies can play an instrumental role in helping managers and team members to "stay close" to each other. Within the CIW NAI team we hope to work with NAI Central to provide fast, geographically independent, secure access to diverse resources ranging from data warehousing to desktop sharing and to scientific instrument control using Virtual Private Networks (VPNs).

Computational collaboration has been enhanced by employing collaborative software development platforms with key features such as enhanced monitoring and reporting capabilities, improved source control and issue tracking integration, flexible workflow capabilities, as well as improved performance through database integration. Over the past five years the CIW IT team has gained significant experience with clustering, distributed computing, and large-scale massively parallel environments, and we recently started experimenting with spanning over Wide Area Networks (WAN), metacomputing systems, and computational grids. This summer, three NAI interns will work with Sághi-Szabó to explore the possible use of Extensible Markup Language (XML) and relational and object-oriented Data Base Management Systems (DBMSs) in scientific knowledge management, organization, and archiving.

7.9 Linkages to Other Agencies

While the NASA Astrobiology Institute provides the primary source of support for research in astrobiology at the Carnegie Institution and for most of the Co-Investigators at partner institutions, there are a number of programs funded by agencies other than NASA or by private sources that support either work on complementary research projects within astrobiology or laboratory instrumentation that will be utilized in NAI-supported measurements (see **Section 10**). Our team's astronomers, for instance, receive now or are currently requesting support from the National Science Foundation (NSF) for extrasolar planet searches (Boss, Butler, and Seager). Co-I Baross derives support from NSF for his oceanographic expeditions to mid-ocean ridge hydrothermal vent sites. Co-Is Emerson, Farquhar, and Hazen are receiving NSF support for research projects distinct from but related to those they are carrying out as part of NAI. The NSF has contributed as well to instrumentation in cosmochemistry, astronomy, and computation that will be utilized on NAI-supported projects. Many of those items of instrumentation were purchased in part with funds from private foundations and individual donors, as well as with institutional funds.