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The Blue Dot Workshop: Spectroscopic Search for Life on Extrasolar Planets

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Table of Contents

Workshop Summary	1
Findings and Research Recommendations	2
Session Summaries	
Biogeochemistry of gases	3
Chemistry and spectroscopy of planetary atmospheres.....	7
Remote sensing of planetary atmospheres and surfaces	11
Workshop Program	15
Workshop Participants.....	17
Abstracts of Workshop Presentations:	
Free Oxygen in the Atmospheres of Mars and Venus	
<i>Mark Allen, Yuk L. Yung</i>	19
Earth's Air Chemistry Seen from Space: Reactions, Timescales, and Notes on Perceived Spectra	
<i>Robert Chatfield</i>	20
Atmospheres and Surfaces of Outer Planet Satellites and other Solar System Curiosities	
<i>Dale P. Cruikshank</i>	22
History of Atmospheric Oxygen Levels	
<i>David J. Des Marais</i>	23
Water on Mars and Venus	
<i>T.M. Donahue</i>	24
Signatures of Intelligent Life	
<i>Frank Drake and Jill Tarter</i>	24
Remote Sensing of Earth's Atmosphere	
<i>C.B. Farmer</i>	25
Radiative Transfer and the Search for Extrasolar Life	
<i>B.D. Ganapol</i>	26
Habitable Zones Around Stars and Their Relationship to CO ₂ , O ₂ , and O ₃ Abundances in Planetary Atmospheres	
<i>James F. Kasting</i>	27
The Project DARWIN	
<i>A. Léger</i>	29
Organic Reactivity Controls on Biogenic Gas Production, Oxidation, and Transport Processes	
<i>Christopher S. Martens</i>	29
Exobiology: Laying the Groundwork in a Search for Extrasolar Life	
<i>Michael Meyer</i>	30

Reduced Biogenic Carbon Gases: Who Cut the Cheese? <i>Ronald S. Oremland</i>	31
Multiple Blue Dots <i>Tobias Owen</i>	32
Remote Sensing of the Earth's Biosphere <i>David L. Peterson</i>	32
Biogenic Trace Gases on Earth: Understanding the Controls on Global Sources and Sinks <i>Christopher S. Potter</i>	33
Contrasts in the Earth's Present and Early Methane Budget <i>William S. Reeburgh</i>	33
How Definitive Would Detection of H ₂ O, CO ₂ , O ₂ /O ₃ and CH ₄ /O ₂ be for the Identification of Life on Planets of Other Stars? <i>Carl Sagan</i>	34
Life Detection by Atmospheric Analysis: Avoiding the Geocentric Bias <i>Andrew Watson</i>	35
A Space-Based, Imaging, Nulling Interferometer: What Can It See? <i>Nick Woolf and Roger Angel</i>	36
Disequilibrium Chemistry by Impacts <i>Kevin Zahnle</i>	39

WORKSHOP SUMMARY

This workshop explored the key questions and challenges associated with detecting life on an extrasolar planet. The workshop included sessions on three related topics: the biogeochemistry of biogenic gases in the atmosphere, the chemistry and spectroscopy of planetary atmospheres, and the remote sensing of planetary atmospheres and surfaces.

The biogeochemistry session reviewed the processes whereby biogenic gases are produced in aquatic environments and on land. Gas production is an unavoidable byproduct of biological oxidation-reduction reactions. Earth's atmospheric composition changed during our biosphere's history, thus the atmospheric "signature" of life which would have been easiest to detect probably also changed. In the early biosphere, mixtures of reduced gases (e.g., H_2S , $(\text{CH}_3)_2\text{S}$, NH_3 , N_2O , methylated halogens, etc.) might have been most distinctive. Later, a mixture of O_2 (and O_3) and these reduced gases would have been most diagnostic of life. Later still, abundant O_2 and O_3 were the most distinctive signatures. Future research should explore the mechanisms whereby the abundances of these gases are regulated. Also, we must better define the composition of a life-sustaining atmosphere in the absence of O_2 .

The atmospheric chemistry session explored scenarios, both biological and nonbiological, whereby an atmosphere might accumulate abundant O_2 , O_3 and H_2O . A Venus-like planet could develop a wet stratosphere, lose its water by photodissociation and subsequent loss of hydrogen, and thus accumulate O_2 abiotically. A Mars-like planet with a magnetic field might accumulate O_2 by long-term hydrogen loss from water dissociation. However, additional critical information about a planet, such as its radius, albedo and effective radiating temperature, could differentiate between O_2 accumulation by these nonbiological mechanisms and O_2 accumulation by life. In addition, in a planet where O_2 had not yet accumulated, session participants concluded that abundant biologically-produced methane might be the most detectable signature of life.

In the third session, the speakers articulated the major challenges associated with the spectroscopic analysis of remote atmospheres. Two strategies were envisioned: analysis of light which passes through the atmosphere of a planet which passes in front of its star (occultation), and analysis of starlight reflected from a planet's atmosphere. The first strategy requires, among other things, a large (~100 meter) space telescope in order to see enough stars. The second strategy calls for a large space-based interferometer to block out the starlight. Future work using interferometry in space will be needed to evaluate interference from dust either in our own solar system or in the target systems.

With the observation that planetary formation is probably a common phenomenon, together with the advent of the technical capability to locate and describe extrasolar planets, this research area indeed has an exciting future.

Findings and Research Recommendations

- * A great diversity of reduced gas species are produced from anaerobic microbial ecosystems. These gases are inevitable byproducts of oxidation/reduction reactions in waters and aquatic sediments.
- * Develop global models for the composition of early Earth's anoxic atmosphere, which existed for hundreds of millions of years or more after oxygenic photosynthesis arose but before atmospheric O₂ accumulated to substantial levels.
- * Define the biological and environmental controls upon the emission of reduced biogenic gases to the atmosphere.
- * Define the controls upon the abundance of atmospheric O₂ on Earth.
- * Document those circumstances where disequilibrium gas mixtures are both truly diagnostic of life and most easily detected.
- * A more conclusive determination of the biogenic origin of atmospheric O₂ in an extrasolar planet requires that abundant H₂O also be detected. Abiotic mechanisms for the generation of substantial O₂ (e.g., a runaway greenhouse) are typically associated with very low H₂O abundances.
- * Substantial abundances of both O₂ and a reduced gas such as CH₄ are strong indications of life. On Earth, biological sources of these gases are much stronger than abiotic sources.
- * The radio search for evidence of intelligent extrasolar life is both a relatively inexpensive and scientifically valid strategy.
- * Effort should be expended to develop both direct (detecting light reflected from or blocked by a planet) and indirect search strategies (detecting motion in a nearby star).
- * Interference from glowing dust in both our own solar system and other solar systems should be evaluated.
- * The stability of stellar emissions and spectra should be evaluated to test the feasibility of evaluating planetary atmospheres during eclipses.

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SESSION SUMMARIES

Biogeochemistry of Gases

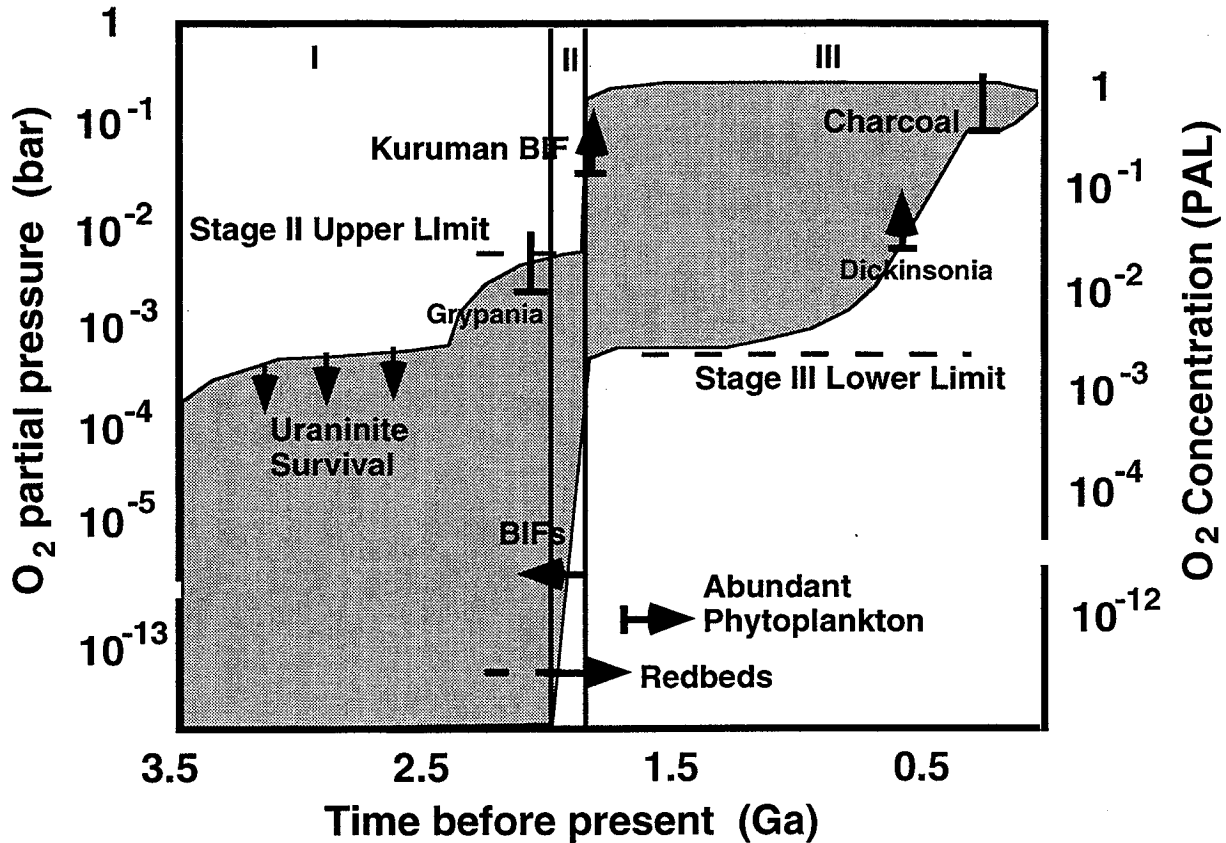


Figure 1. Estimated changes in atmospheric O₂ levels during the history of the Earth. Adapted from J.F. Kasting, *Science* 259, 920-926, 1993.

The history of biological contributions to Earth's atmosphere provides insight for structuring a search for life on extrasolar planets. Our own biosphere is older than 3.86 billion years, which is more than 85 percent of Earth's lifetime. Life has had to adapt to the evolution of the global environment, and the composition of Earth's surface and atmosphere has changed over time. Accordingly, a flexible and effective strategy to search for an extrasolar biosphere should take into account the full spectrum of compositions which might have existed during the history of our own biosphere.

For purposes of illustration, three distinct stages in our biosphere's evolution are envisioned. The first stage is the interval between the origin of life and the development of oxygenic photosynthesis. The atmosphere was at least mildly reducing and was dominated by CO₂, N₂, H₂ and H₂O. The modest amounts of O₂ created by the photodissociation of water vapor and loss of H₂ to space were largely consumed by reactions with reduced gases and aqueous species delivered by volcanoes and hydrothermal activity. The earliest biosphere depended upon these nonbiological sources of reducing

power for the synthesis of organic compounds. Anaerobic microbes dominated the biosphere's contributions to the atmosphere. Some of the key gas-forming microbial processes involved redox reactions, including the synthesis and the degradation of organic compounds. Such processes included methanogenesis, dismutation reactions with carbon and sulfur, anoxygenic photosynthesis, oxidation and reduction of nitrogen species and acetogenesis. These processes created CH₄, larger hydrocarbons, CO, H₂S, (CH₃)₂S, NH₃, N₂O, methylated halogens and a host of other less abundant, reduced trace gases. The biogenic signature of an atmosphere might consist of a suite of reduced gases whose abundance and diversity are much greater than those in the atmosphere of a lifeless planet.

The second stage of our biosphere's evolution represents the time interval between the evolution of oxygenic photosynthesis and the accumulation of a substantial inventory of oxygen (>0.1 percent by volume) in the global atmosphere and ocean. The advent of oxygenic photosynthesis very likely increased gross global biological productivity by a factor of 100 or 1000. Even so, perhaps hundreds of millions of years were required before the net production of O₂ exceeded the output of reduced volcanic and hydrothermal gases, allowing O₂ to become a dominant atmospheric constituent. During this interval, the atmosphere displayed a very diagnostic biological signature, namely a disequilibrium mixture of reduced gases and O₂.

The third stage encompasses the interval (the past 1.8 to 2 billion years on Earth) where O₂ became a major atmospheric constituent (>0.1 percent by volume). Its production and consumption were dominated by biological processes. Anoxic environments retreated to localities (e.g., fine-grained aquatic sediments, hydrothermal systems, etc.) where they were maintained by local sources of reducing power (e.g., organic decomposition, volcanism). Accordingly, atmospheric concentrations of reduced biogenic gases declined to trace levels. For example, the concentration of CH₄, which is currently the most abundant reduced biogenic gas, is only 1.7 parts per million by volume. Thus, O₂ and O₃ are the most easily detected biogenic gases during this most recent stage.

The above short overview offers several insights. First, life can begin very early in a planet's history. Thus, a planet whose environment is suitable for a biosphere probably developed life relatively quickly. Second, O₂ is not necessarily an atmospheric component shared by all biospheres. Earth required at least 2 to 2.5 billion years of evolution before accumulating an abundant O₂ inventory. Also, even though oxygenic photosynthesis confers substantial advantages for the biota, its development might not necessarily be an inevitable consequence of biological evolution. Third, other reduced gas species are highly diagnostic of life, but their detectability might be constrained by their low concentrations. However, atmospheric budgets of most reduced biogenic gases have not been modeled in O₂-free atmospheres.

Future research should explore the processes responsible for creating unambiguous atmospheric signatures of life. For example, we are still uncertain as to why our own atmospheric O₂ inventory is currently maintained near the 21 percent level. Today, O₂ and its byproducts participate in the destruction of most, if not all, of the reduced biogenic gases. The atmosphere, both of early Earth and, perhaps, of some of the other inhabited planets, had low O₂ contents. Therefore the budgets of reduced gases such as volatile hydrocarbons, sulfides, amines and NO_x should be modeled in low-O₂ atmospheres. Such modeling should explore atmospheric compositions under at least the following two scenarios:

1) Oxygenic photosynthesis exists but the volcanic sinks for O₂ are stronger than they are presently on Earth, and 2) Oxygenic photosynthesis does not exist, therefore biological primary productivity is maintained either by abiotic sources of reducing power or by other mechanisms not employed in our own biosphere.

Regarding future research simple ecosystems of bacteria should be manipulated in order to ascertain the various controls upon gas production. For example, the effect of different levels of O₂ and alternative electron acceptors can be evaluated. Such work should be done in collaboration with atmospheric chemists who could evaluate how the gases produced by such ecosystems might be modified subsequent to their emission.

We should define the circumstances under which disequilibrium mixtures of atmospheric species indeed indicate life's presence. Under which circumstances are disequilibrium gas mixtures produced which are both truly diagnostic of life and most easily detected?

Chemistry and Spectroscopy of Planetary Atmospheres

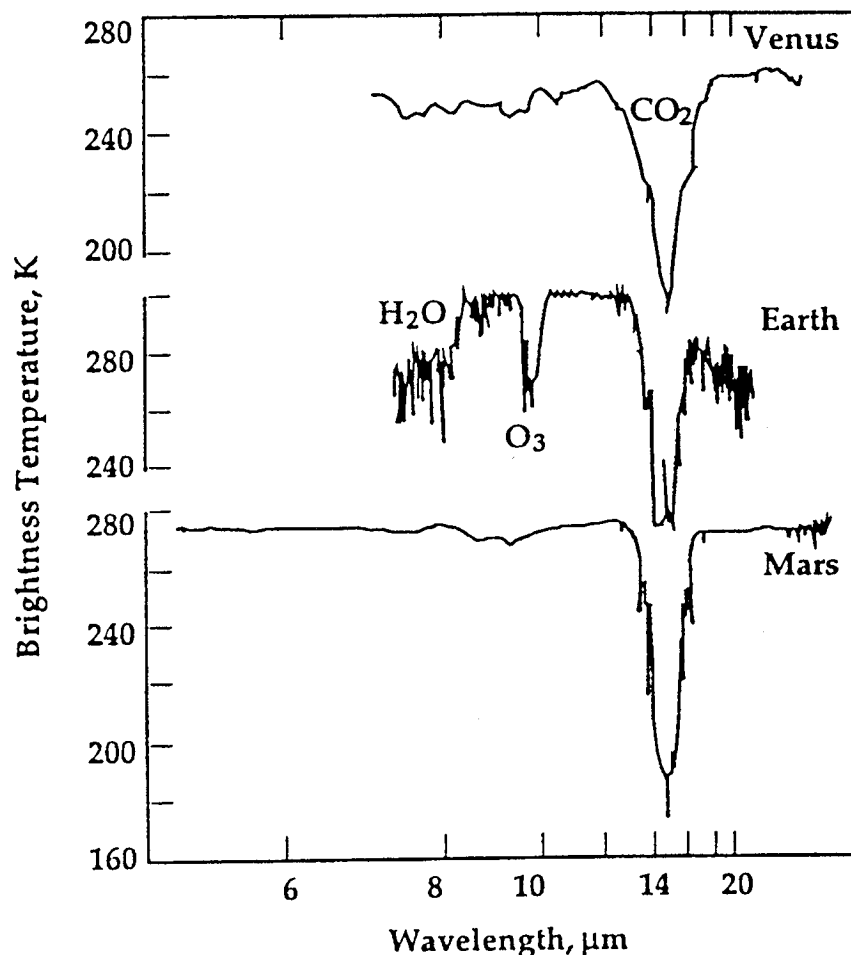


Figure 2. The spectrum of Earth is contrasted with that of Venus and Mars (from "A Road Map for the Exploration of Neighboring Planetary Systems," C.A. Beichman, ed., JPL Publication 96-22, 1996).

What gases would we expect to find in an Earth-like extrasolar planet atmosphere and what might their detection tell us about the presence of life on that planet? These questions overlap strongly with those discussed in the other sections of the workshop. Here, though, the emphasis was primarily on the chemistry and physics of planetary atmospheres, as opposed to biology or astronomy/remote sensing.

A very specific question addressed in this session, but one which is central to the problem of detecting extrasolar life, is the following: Would the detection of measurable amounts of ozone (O_3) in a planet's atmosphere be considered evidence for life? The argument is based on the fact that O_3 is produced photochemically from O_2 , and the strongest source of the O_2 in Earth's atmosphere is photosynthesis. So, another way to word this question might be: What are the possible abiotic sources for O_2 , and could such abiotic sources result in measurable amounts of O_2 and O_3 in a planet's atmosphere?

A consensus emerged from those present at the workshop that useful information about the existence of extrasolar life might be obtained from measurements of O₃. However, workshop participants stopped short of saying that the presence of O₃ was, by itself, a definitive indicator of life. Furthermore, it was pointed out that there are at least two clearly identifiable circumstances in which substantial amounts of O₂ and O₃ might be produced abiotically. To show what these circumstances are, and to show how the workshop participants arrived at this conclusion, let us briefly review the assumptions that were made.

First, we assumed that it was theoretically possible to observe spectroscopically the presence of at least three gases in the atmosphere of an extrasolar Earth-like planet: H₂O, CO₂, and O₃. All three gases have strong, clearly identifiable absorption bands in the thermal infrared between 6 μm and 17 μm. Other biogenic trace gases, such as CH₄ and N₂O, have weaker absorption features within this spectral region and, hence, would be much harder to observe. This is unfortunate because the participants agreed with the idea expressed originally by Lovelock that an optimal remote life detection method would be to look for the simultaneous presence of O₂ and a reduced gas, such as CH₄. But we assumed that it would not be possible to do this with a first-generation extrasolar planet telescope.

We also assumed that it would be possible with the same first generation telescope to obtain estimates for an extrasolar planet's radius (R), albedo (A), and effective radiating temperature (T_e). T_e is obtained from the slope of the observed infrared emission curve. Then, R can be determined from the area under the curve, i.e., the total infrared flux (F), by using the Stefan-Boltzmann Law: $F = \sigma T_e^4$, where σ is the Stefan-Boltzmann constant. Finally, A is determined from the principle of planetary energy balance (absorbed stellar radiation = emitted infrared radiation), using the observed distance of the planet from its primary and the known luminosity of the star.

The additional physical information about an extrasolar planet is considered critical in understanding the possible significance of the detection of O₃ in its atmosphere. The presence of H₂O bands in a planet's atmosphere, combined with knowledge of the amount of stellar radiation it absorbs and its effective radiating temperature, should provide a good indication of whether liquid water exists at the planet's surface. Liquid water is considered essential for life as we know it. This direct information about the presence of water would augment purely theoretical estimates of whether the planet orbited within the star's liquid water habitable zone, or HZ. (See abstract by Kasting and references therein, this volume.)

For a planet with a predominantly nitrogen atmosphere within the HZ around a star, it was generally agreed that there is no known abiotic mechanism for producing large amounts of O₂ and O₃. In an atmosphere with a terrestrial-like thermal structure, the production rate of O₂ from photodissociation of H₂O is relatively small because the stratosphere is relatively dry. O₂ would be consumed by reaction with reduced volcanic gases and by liquid water-mediated reactions with reduced materials (Fe²⁺, S²⁻, organic C) at the planet's surface. Photochemical model calculations predict that atmospheric O₂ concentrations would be much too small to produce an observable amount of O₃ under these circumstances.

Several workshop participants (e.g., Léger, Allen, Kasting) pointed out that planets lying close to or within the HZ need not obey the same rule if the dominant atmospheric constituent is CO₂.

Depending on a number of factors, photodissociation of CO_2 can produce significant O_2 and O_3 mixing ratios. The abundances of these free oxygen species will be modulated by the presence of H_2O and the consequential catalytic hydrogen photochemistry. An additional source of oxygen may result from the photodissociation of water and the escape of hydrogen to space. Planets like Venus that receive too much stellar radiation can develop wet stratospheres in which H_2O is rapidly photodissociated. Consequently, they may lose hydrogen to space at a rapid pace, building up O_2 in the residual atmosphere. Planets like Mars that are too cold at their surfaces to maintain liquid water and too cold inside to maintain active volcanism, could also accumulate O_2 -rich atmospheres over time as a result of more gradual hydrogen loss. This would be especially true if the planet were slightly larger than Mars and had an intrinsic magnetic field, so that it did not lose oxygen by nonthermal escape mechanisms, such as dissociative recombination of O^{2+} and solar wind sputtering. Such Mars-like and Venus-like planets could presumably be identified from knowledge of their effective radiating temperatures and from measurements of H_2O absorption within their atmospheres.

Thus, the detection of O_2 and O_3 on extrasolar planets, in the absence of the detection of other key species, is likely to present ambiguous evidence for the presence of life. However, in principle, we could distinguish between abiotic and biotic sources of free oxygen with additional observational data, for example, temperature and abundances of H_2O and CO_2 .

In addition to the interest in O_2 -rich atmospheres, it was noted that some planets might resemble the Archean/Early Proterozoic Earth (3.8-2.2 Ga), which is thought to have been inhabited by microbial life, but on which the atmosphere remained essentially O_2 -free. Earth's atmosphere during this time period may have contained several hundreds of ppm of CH_4 , most of which was produced by methanogenic bacteria. These large amounts of CH_4 should be readily observed spectroscopically with the same first-generation space telescope that would be used to look for O_3 . The presence of CH_4 in a planet's atmosphere would not be unambiguous evidence for life, as it is possible that this methane could have been supplied by volcanic outgassing at submarine hydrothermal vents. Nevertheless, biological methane sources are considerably larger than abiotic ones, so the abundance of CH_4 in a planet's atmosphere may provide some strong hints as to whether life is present.

Remote Sensing of Planetary Atmospheres and Surfaces

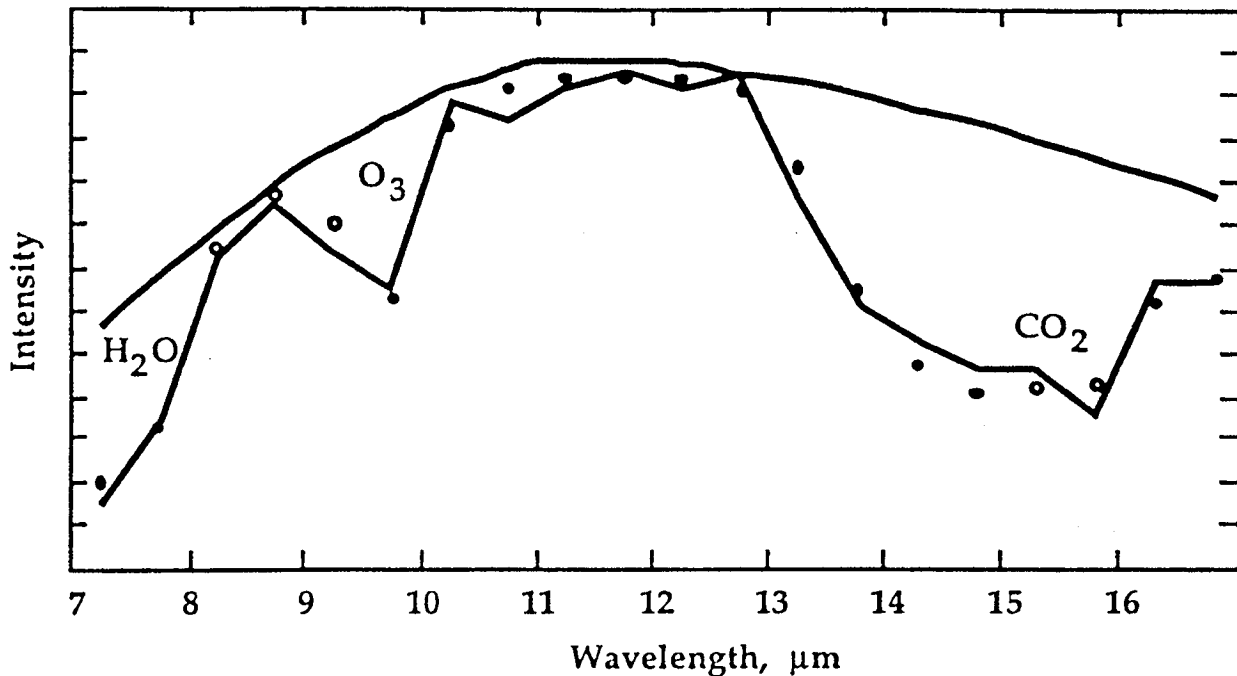


Figure 3. The spectrum of an Earth twin after 6 weeks of integration (from "A Road Map for the Exploration of Neighboring Planetary Systems," C.A. Beichman, ed., JPL Publication 96-22, 1996).

This session dealt with how we would observe planets to find whether they are present, whether they are habitable like Earth, whether life has developed on them, and whether they have developed intelligent life. These questions are arranged sequentially such that any positive answer further along the chain probably requires a set of positive answers to all the prior questions too. However, a negative answer at any point does not imply that answers to previous questions are negative.

Spectroscopic studies of other planets in our Solar System have already started. However, these planets are sufficiently close that we cannot exclude the possibility that microbial life has traveled from one to another. On the other hand, interstellar distances are so great that the presence of life on other solar systems implies either independent origination, or some type of panspermia process on a large scale.

Radio Searches

The examination of possibilities for searching other systems broke into two fundamentally different categories. Testing for certain types of intelligent life, which might mimic our own behavior, is currently being done and is the only study within this group that is presently possible. It is also possible at relatively modest cost. The Galileo flyby of Earth demonstrated that even close to Earth, only radio observations of communications signals gave totally unambiguous indications of life here. The remote sensing group at this workshop felt that the results from radio studies (like SETI) were

of compelling interest and asked the entire conference to endorse the method and current programs as valid scientific work. However, regardless of the outcome of the SETI study, it enters the problem so far down the chain of inference (see first paragraph above), that additional searches addressing the frequency of planets, the frequency of habitable planets, and the fraction of these on which unintelligent life has developed are needed to build the science of searching for life on a sound foundation.

Optical/Infrared Searches

i) Indirect searches. Optical/Infrared searches for planets can either be direct, which is seeing radiation emitted, absorbed or reflected by a planet, or indirect, in which the gravitational pull of a planet on a star causes the star to perform a miniature orbital motion. This motion can be sensed either by its effect on the speed of the star in the direction of the line of sight, or on the movement of the star in the plane of the sky. Both techniques have already proved successful in finding the first few planets around other stars. The status of the techniques is that if either were applied to the Sun at the performance level now applied to other stars, and from a reasonable distance (more than 5pc), no planets would be detected. The techniques depend on the movement of the star not being confused with processes (starspots, prominences, faculae, granulation etc.) which vary the brightness over the surface of a star, and therefore make its light-center an inadequate measure of its center of mass. The evidence available today suggests that these effects will make the detection of extrasolar Earth-sized planets extremely difficult. Whether or not the searches become impossible is disputed.

ii) Direct searches. Searches for planets can be made by attempting to detect the radiation either reflected or emitted from the planet. Earth's emission is most visible at infrared wavelengths where it emits about 1 part in 10 million as much as the Sun.

If the orbit of the planet passes through the line joining the star to the Earth, then once each orbit, the planet will eclipse (occult) the star. Earth eclipses of the Sun cut out about one part in 10,000 of the Sun's light for a total of 10 hours every year. It is also possible to search for these eclipses as direct evidence of the presence of planets. Such searches do not seem practicable on Earth, because of weather and other atmospheric effects, but they are possible from space. In space, the topic of debate is not so much whether the measurements can be made, but the size and cost of the operation to make such observations, and how, with the delays inherent in sending up space telescopes, they fit into a program to observe external planets.

Spectroscopic studies of the atmospheres of planets are in principle possible for either of these processes. In eclipse, only the part of a planet's atmosphere beyond the limb and contributing to the eclipse, affects a star's spectrum. Thus we would be trying to see optical features with a maximum possible depth of about 3 parts in 10 million of starlight. For looking straight at the planet, the depths are 100%, but in 1 part in 10 million of the star's radiation.

Direct versus Indirect Searches

Among the differences between these two methods are the following: 1) It is possible to blot out the starlight while still seeing the planet in the second observation, but not possible to blot out the starlight because we must observe the eclipse for the first kind of observation. 2) Because typically

only 1 in every 200 Earth-like planets will show an eclipse, studies of eclipses will typically look at stars (200)^{1/3} further away, and they will be about 35 times fainter than non-eclipsed counterparts.

The technical problems of either observation are acute. To see planets by their own radiation requires an interferometer to blot out the starlight. This technique has not been used previously and it stretches our current technical abilities. The device must operate in the infrared where both the Solar System dust and the telescope glow. The telescope must be sent out to about 5 Astronomical Units at a site where the dust and telescope glow less because they are colder. The device would consist of four telescopes each of about 1.5 meters diameter and aligned in a linear array 75 meters long.

The eclipse measurements must be made with a supergiant space telescope, probably over 100 meters in diameter, in order to see enough stars. Because only a few ten millionths of the radiation would be affected by planetary atmosphere absorptions, detection to this precision would require CCD detectors with very perfect surfaces. The required storage per resolution element of 50 bits, together with the necessary transfer between the CCD and the computer, including the A-D conversion, would be challenging.

Beyond these technical issues are astronomical unknowns. For seeing planets' radiation, how badly are we bothered by glowing dust in the planet's own system? For the eclipse studies, how stable is the spectrum of a sun-like star which has those atmospheric disturbances previously mentioned? It is in principle possible to overcome external dust by building a larger interferometer with larger mirrors. But it would be good to know if this is needed before sending a spacecraft on this long journey. If a star's spectrum is not sufficiently stable, the eclipse technique fails and does not seem to be curable.

What might be seen?

A first generation interferometer to observe planets would see water and carbon dioxide easily, and if the O₃ levels are like the Earth's, O₃ will be observable but harder to see. The interferometer will detect a planet's radiation, derive a color temperature for the emitting region of its surface or atmosphere, and determine how far the planet is from its star. To detect the next most significant molecule, methane, will require telescopes 100 times larger in area. Nitrous oxide needs an even larger telescope. An ultra-large telescope to observe eclipses would see the molecular oxygen A band. There are water and carbon dioxide features in the same spectral range, but they are very weak. The limits of performance would likely be set by intrinsic star spectral noise. The distance of the planet from the star could be determined from the planet's period, but there would be no independent evidence of temperature.

Additional Recommendations

The study of planet spectra during occultation is a very new possibility. Although some aspects mentioned here appear to be not very encouraging, only a more detailed study can reveal the true size of the problems and the possible solutions. Investigation of possible occultation strategies by FRESIP-style space observatories is worth continuing.

The potential studies that are needed to make space infrared interferometry into a practical tool include flying an optical interferometer, flying an infrared interferometer to detect dust around other stars and flying a probe of the radiation from the zodiacal dust of our own system. All these possibilities are discussed in the EX-NPS final report by NASA. We support such work.

Blue Dot Workshop Program

Thursday

Introduction: context of this workshop

9:00 AM	Organizing committee	Welcome, logistics
9:15	Black, David	The Origins Vision: A context for the search for extrasolar life
9:45	Meyer, Michael	Exobiology: Laying the groundwork in a search for extrasolar life

Biogeochemistry of gases

10:15 AM	Des Marais, David	History of earth's atmospheric O ₂ levels
10:45	Martens, Chris	Organic reactivity controls on biogenic gas production, oxidation, and transport processes
11:15	Oremland, Ronald	Reduced biogenic carbon gases: who cut the cheese?
11:45	Reeburgh, Bill	Sources and sinks of biogenic reduced gases

12:15 PM *Lunch*

1:30 PM	Potter, Chris	Global modeling of biogenic trace gases
2:00	Chatfield, Bob	Trace gases in earth's atmosphere: reaction networks
2:30	Watson, Andrew	Possible atmospheric signatures of life: avoiding the geocentric bias
3:00	<i>Break</i>	

Chemistry and spectroscopy of planetary atmospheres

3:30	Léger, Alain	Life signatures in a planet atmosphere
4:00	Allen, Mark	O ₃ , O ₂ and disequilibrium chemistry in planetary atmospheres
4:30	Kasting, Jim	Habitable zones around stars and their relationship to CO ₂ , O ₂ , and O ₃ abundances in a planet's atmosphere
5:00	Donahue, Thomas	Water on the terrestrial planets, young and old
6:00	<i>Cocktail hour, Michael's Restaurant</i>	
7:00	<i>Banquet, Michael's Restaurant</i>	

Friday

Chemistry and spectroscopy of planetary atmospheres (continued)

8:30 AM	Owen, Tobias	Multiple blue dots: How to tell giants from dwarves
9:00	Cruikshank, Dale	Atmospheres of the moons of the outer planets
9:30	Zahnle, Kevin	Disequilibrium chemistry by impacts
10:00	Sagan, Carl	How definitive would detection of CO ₂ , H ₂ O, CH ₄ and O ₂ /O ₃ be for the identification of life on planets around other stars?
10:30	<i>Break</i>	

Remote sensing of planetary atmospheres and surfaces

10:50 AM	Peterson, David	Remote sensing of Earth's modern biosphere
11:20	Ganapol, Barry	Modeling atmospheric radiative transfer
11:50	<i>Lunch</i>	
1:00 PM	Farmer, Barney	Remote sensing of earth's atmosphere
1:30	Woolf, Neville	A space-based, imaging, nulling interferometer: what can it see?
2:00	Drake, Frank	Signatures of intelligent life

General Discussion

2:30 PM	Discussion strategy	
2:40	<i>Break</i>	
3:00	Discussion groups	
	Biogeochemistry	
	Atmospheric chemistry and spectroscopy	
	Remote sensing of atmospheres and surfaces	
4:00	Plenary session	
5:30	Adjourn	
6:00	<i>Reception, SETI Institute</i>	

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ABSTRACTS

Free Oxygen in the Atmospheres of Mars and Venus

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The study of the terrestrial planets has provided an opportunity to understand the factors controlling the abundance of free oxygen—primarily O₂ and O₃—in abiotic atmospheres. This experience should be able to guide future assessments of detections of free oxygen in extrasolar planetary atmospheres with regard to the relative contributions of biotic and abiotic processes.

Both Venus and Mars have atmospheres dominated by CO₂. In the latter, O₂ has been measured to have a fractional abundance of 10⁻³ and O₃ a fractional abundance of 10⁻⁸ (column average). However, in the former, there is only an upper limit to O₂ of 3 x 10⁻⁷.

The observations of O₂ and O₃ in the Martian atmosphere may be reproduced by an atmospheric model with only gas-phase chemistry, surface/atmosphere exchange buffering the level of CO₂ and H₂O, and exospheric escape of atomic H, H₂, and atomic O (Nair, *et al.*, 1994). The good agreement between model and measurements was achieved by varying literature-recommendations for rate coefficients within their uncertainties and adopting a high oxygen loss from the atmosphere (to space or to the surface). This study highlights the need for a detailed understanding of kinetic rate coefficients, surface/atmosphere interactions, and planetary escape rates before one can simulate quantitatively atmospheric composition. Accepting that we have a correct model for the processes controlling Martian atmospheric species abundances, we then can use this model to explore the abundance of O₂ in a Mars-like atmosphere, but under different physical conditions. One test run with this model—for a completely dry atmosphere at current pressure and temperatures—yields an O₂ fractional abundance as high as 4 x 10⁻². In this case, the O₂ level is controlled by the slow recombination of O and CO to reform CO₂. Since this reaction has a temperature dependence of exp(-2184 K/T), we would expect a colder atmosphere to have an even higher O₂ level. Other scenarios may lead to high O₂ abundances depending on variations in the relative rates of H and O escape.

The abundance of O₃ in the Martian atmosphere is directly related to the level of O₂. In the current epoch the abundances of free oxygen are regulated by catalytic cycles involving HO_x species. Nair, *et al.*, (1994) show the derivation of an algebraic expression that describes the O₃/O₂ relationship in terms of kinetic and photolytic rate coefficients, abundances of major and minor species, and the escape flux of O. Consequently, from observations of O₃, along with measurements of physical conditions and other composition variables, one can infer the abundance of O₂.

The Venus atmosphere presents a contrasting situation of a highly oxidized atmosphere with little free oxygen. In current models (Yung and DeMore, 1982; Krasnopolsky and Parshev, 1983), the CO₂ atmosphere is stable and the O₂ level is a balance between CO₂ photolysis and catalytic cycles involving HO_x and ClO_x species, with the relative importance of the different processes still to be

confirmed. However, the O₂ abundance in these models is ten times the observational upper limit for this species. Further progress in understanding the level of free oxygen in Venus will require more observations and more laboratory measurements of rate coefficients for potentially important reactions.

From the combined experience of modeling free oxygen in the atmospheres of Mars and Venus, we suggest that the abundance of free oxygen in an abiotic atmosphere may be simulated with reasonable accuracy if key physical and chemical observations and laboratory measurements are available. In addition, simple relationships between O₂ and O₃ can be devised. In conclusion, if appropriate observations of an extrasolar planet were to be available, it should be possible to assess whether the detected free oxygen levels were solely controlled by abiotic processes or, in the absence of a good simulation on that basis, whether biotic processes might be actively influencing atmospheric composition.

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Earth's Air Chemistry Seen from Space: Reactions, Timescales, and Notes on Perceived Spectra

Robert Chatfield, NASA Ames Research Center

This is an attempt to survey the important radiatively active chemical species of the Earth's atmosphere as they might be perceived from distant space. While the distances involved imply that only half-disk reflected solar (stellar) radiation and full-disk thermally emitted radiation can be seen, the diurnal rotation of Earth would reveal some additional information, especially for species with reaction time-scales of 10-100 days like carbon monoxide. The survey progresses in order of descending mean atmospheric concentration, though mean concentration has only weak correlation with radiative signal until we reach the 10 ppb mixing-ratio level. For example, molecular oxygen (O₂ 0.21 molecular ratio) may be marginally observable in the 1.2 mm reflected solar spectrum, while ozone (with the global equivalent concentration of 500 ppb) should be visible at many wavelengths, especially the strong 9.6-mm band. It would be more visible than oxygen in the reflected solar spectrum, in the Chapuis bands. A significant indicator of Earth's oxidant chemistry is the O₃/O₂ ratio, set to 2×10^{-6} . This value is essentially set by the Chapman ozone chemistry, and N/S differences are mostly determined by the arrangement of continents and especially mountains, which

determine the transport of ozone in the slow-chemistry regions of the lower stratosphere. Effects of other catalytic ozone-destruction cycles would therefore be difficult to infer.

Carbon dioxide and water would also be easily detectable in the infrared. Given the right viewing geometry, the annual variation in the northern hemispheric abundance of CO₂ would be visible, since the variation runs to about 15 ppm out of 340 ppm, or 5 %. The mean abundance of methane (1.7 ppm) should be visible, but annual variations would be only a few percent with a smaller usable methane emission signal.

Nitrous oxide, at 300 ppb, might well be distinguishable in thermal IR spectra, though its ca. 300 year atmospheric lifetime implies that it is thoroughly mixed up to the tropopause. Detecting nitrous oxide's spectrum would require finesse, since its major CO₂-window emissions tend to be overlapped by methane. Methane and nitrous oxide would be particularly likely emissions in a living planet. Nitrous oxide would appear to accumulate in the atmospheres of planets with remotely Earth-like living conditions. That species (and maybe NO, nitric oxide) seem to be emitted due to multiple leaks in the redox chemistry performing the interchange of two vital forms of nitrogen in Earth-like living systems: ammonium and nitrate; terrestrial experience suggests that the intermediate +1/2 oxidation state cannot be bypassed completely, and so small leaks of the gas occur. The long lifetime of N₂O makes the gas observable. Somewhat similar arguments can be made for the "natural" tendency to emit methane in the redox environment of Earth-like life. For sulfur gases, the only accumulating analog is OCS, with approximately one-thousandth the concentration; what we know of the OCS emission process makes it appear more peripheral to vital biogeochemical processes.

Carbon monoxide is a fascinating species that could be observed. Its intermediate lifetime, due to OH concentrations averaging 10⁺⁵, means that it often has a longitudinal variation that would be seen from space as a diurnal variation in radiance of a factor of 2 to 3 (as shown by the NASA Langley MAPS instrument). The variation arises from the fact that many CO sources (biomass burning, the oxidation of natural and anthropogenic organic emissions) are strongly tied to the Earth's pattern of continents and oceans. Earth's continents are brighter than its dark oceans, so high CO would be correlated with high continental albedo. One difficulty is that the longitudinal variation of cloudiness and water vapor tend obscure CO's signal. Since prolonged averaging might be necessary to observe CO's relatively weak thermal IR features, time-aliasing techniques might be necessary to see the diurnal variation. Observation of the annual cycles of CO might be more feasible.

Other organic emissions include isoprene and the natural vegetative emissions, which rival or outweigh methane in contribution to the global carbon cycle. In total, CH₄, CO, and these natural organics contribute only a few percent of the larger CO₂ carbon cycle. The emissions of these natural organics appear to be highly specific to certain vascular plants, in distinction to the emission of CH₄ and N₂O. C₂ and C₃ non-methane hydrocarbons might accumulate to concentrations higher than their ppb levels in an Earth-like atmosphere with less OH. Acetone, with its clear carbonyl band, might be most visible; current concentrations are around 1 ppb. However, at some point, perhaps with OH at 10³ or higher, there would likely be competition in the oxidation/removal process from the halogen-based radicals Cl and BrO. On Earth, these arise from acid-displacement of Cl and other volatile halogen compounds from sea salt, but also might result from photochemical processes, especially in low-OH atmospheres. Methyl halides could also accumulate to some extent, but become susceptible

to UV radiation in low-ozone atmospheres, and this process could contribute even more halogen radicals.

Atmospheres and Surfaces of Outer Planet Satellites and other Solar System Curiosities

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IR spectroscopy of Triton, Pluto, its satellite Charon, and an important planet-crossing body (5145 Pholus) opens a window on the compositions of these primitive members of the population of left-overs from the epoch of planet formation. Current results of the spectroscopy (0.4-2.5 μm) of these bodies and other planetary satellites are summarized:

Pluto (Pale Pink Dot) Surface: Near-IR spectroscopy shows that Pluto has a mostly icy surface dominated by N_2 , with CH_4 , CO , and H_2O detected. There are a few other weak spectral features that have not been identified. Dark regions are probably covered with organic solid material, as yet unidentified, and with no clear spectral features. Atmosphere: N_2 -dominated, probably in vapor-pressure equilibrium at $T=40\text{ K}$ ($\sim 57\text{ }\mu\text{bar}$) CH_4 probably detected, CO being sought. Atmospheric pressure probably changes with heliocentric distance; presently near maximum.

Pluto's satellite Charon (Pale White Dot) Surface: H_2O ice appears to dominate the surface, but other ices and refractory solids may exist. Atmosphere: None detected, but N_2 , CO , CH_4 possible.

Triton (Pale White Dot) Surface: This satellite of Neptune is spectrally similar to Pluto, with an icy surface dominated by N_2 , CH_4 , CO , CO_2 , and H_2O . Isotopes of C (and possibly O) are detected. Atmosphere: N_2 atmosphere detected by Voyager; vapor-pressure regulated, $P_s = 16\text{ microbar}$. No CH_4 or CO yet detected, but currently being sought. Photochemical haze observed by Voyager, plus plumes of particles (and gas?) rising from surface. Sublimation wind flowing from S. pole northward detected.

5145 Pholus (Pale Red Dot) Surface: Pholus has a very red reflectance in the photovisual region, H_2O ice bands at 1.6 and 2.0 μm , plus a strong absorption band at 2.27 μm attributed to combinations in C-H bands in organic solids, probably light hydrocarbons ($< 400\text{ amu}$; e.g., methanol, hexamethylenetetramine). Atmosphere: None detected. Cometary activity possible in the future.

Jupiter's Satellite Io: (Bright Orange Dot) Atmosphere: Transient tenuous atmosphere of SO_2 , which in part freezes on surface, and part of which is swept away by the plasma flow. P_s a few microbars at most.

Jupiter's Satellite Ganymede: Surface: Mixture of H_2O ice and rocky material. O_2 detected in ice, induced by charged particle bombardment. Atmosphere: None detected.

Jupiter's Satellite Europa: Surface: Dominated by nearly pure H₂O ice. Hubble Space Telescope UV spectra show a feature tentatively attributed to solid O₃ generated in the ice.

Saturn's Satellite Titan: (Pale Orange Dot) Atmosphere: N₂ + CH₄, with P_s 1.5 bar. Rich hydrocarbon inventory in stratosphere. Nearly opaque organic haze with color/optical properties matching organic solids (tholins) produced by plasma discharge in lab mixture of N₂:CH₄ = 9:1.

History of Atmospheric Oxygen Levels

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The key O₂ sources are O₂-producing (oxygenic) photosynthesis accompanied by burial of photosynthetic organic matter, and the photo-dissociation of water vapor and the loss of hydrogen to space. Key O₂ sinks are biological O₂ respiration, reduced volcanic gases, and weathering of rocks containing reduced elements such as carbon, sulfur and iron.

Before oxygenic photosynthesis arose, the relatively minor O₂ source of water vapor photodissociation was overwhelmed by abiotic and biotic fluxes of reduced species. Oxygenic photosynthesis appeared after a succession of diversifications in the light-harvesting reaction centers of photosynthetic bacteria finally led to cyanobacteria. These diversifications were driven by competition both for reduced species for organic synthesis and for various wavelengths of light. Oxygenic photosynthesis provided a virtually unlimited supply of reducing power. Life could exist anywhere that light, liquid water, nutrients and a stable substrate were available.

Oxygenic photosynthesis arose long before O₂ became abundant in the atmosphere. Fossil evidence of cyanobacterial ecosystems appeared before 3.0 billion years (Ga) ago. Sulfates (at 3.4 Ga) and oxidation of organic matter (3.0 Ga) indicate that O₂ was present locally around photosynthetic ecosystems. Atmospheric O₂ levels rose substantially between 2.2 and 2.07 Ga. Oxygen-sensitive detrital minerals (FeS₂, UO₂) disappeared, iron was retained as Fe³⁺ in soils, and redbeds and O₂-requiring eukaryotes arose. Banded iron formations, Fe²⁺-rich finely-laminated deposits, disappeared by about 1.8 Ga, indicating that O₂ had finally permeated the deep oceans.

The history of O₂ increases reflects planetary and biological change. Sources of O₂ strengthened. Oxygenic photosynthesis evolved; cyanobacteria proliferated over widening continental shelves; and plankton arose. Stabilized continents enhanced the preservation of photosynthetic organic carbon. Sinks of O₂ weakened, as fluxes of reduced volcanic species (H₂, Fe²⁺, sulfides, etc.) decreased.

Earth's history offers insights for a survey of extrasolar planets. Life arose very early and depended upon reduced volcanic emanations. Even after oxygenic photosynthesis arose, perhaps 1 Ga or more passed before O₂ became a substantial atmospheric constituent. A dependable O₂ supply was essential for the development of complex (plants and animals) and intelligent (us?) life.

Water on Mars and Venus

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This paper reviews evidence relating to the abundance of water on early Mars and Venus from measurements of the present abundance of hydrogen compounds, deuterium to hydrogen (D/H) ratios and escape fluxes. For Mars, recent measurements of D/H ratios in SNC hydrous minerals provide data on the ratios at earlier times to augment present atmospheric values. Interpretation of these data shows that they are consistent with the presence of scores to hundreds of meters of liquid water on early Mars. In that case, they also require concentrations of hydrogen compounds in the early atmosphere orders of magnitude higher than at present. For Venus, a very large D/H enhancement (160 fold) implies at least 3 to 4 meters liquid equivalent of early water (depending on how much hydrogen is in the atmosphere today). It is consistent with much more, even the equivalent of a full terrestrial ocean. The low escape flux and high fractionation factor place severe constraints on volcanic or cometary sources. Some of the present water can have been injected by volcanism but comets as important sources appear to be excluded.

Signatures of Intelligent Life

Frank Drake and Jill Tarter, SETI Institute

Plausible observable products of reasonable technologies are examined. It is obvious that many possibilities, such as particle beams, are very unpromising candidates for detection. Electromagnetic radiation is most promising, but as is well known, the shortest and longest wavelengths are unpromising because of physical and galactic barriers to their detection. The optical radiation of the contemporary human civilization is shown to be very difficult to detect. As has been concluded for some 35 years, microwave transmissions are by far the most promising signatures to search for. Their striking power, compared to, say human light emissions or even stellar radio emission, makes them promising. Quantitative comparisons are given (see next page), showing very large advantages in signal power for the microwaves. Furthermore, the intelligent, therefore biological, origin of microwave signals is readily and definitively established. This is manifest in the sharply defined bandwidth in which signals will likely occur, the fact that they will very likely be highly polarized, and the fact that they will likely exhibit a well-defined and "unnatural" modulation.

It would appear that the search for intelligent radio signals is an extremely promising, relatively inexpensive, means to search for biology in space. However, political opposition will probably cause such searches to continue to be supported entirely by private contributions.

Comparison of Power Levels for an "Earth-Sun-like" Pair

For an Earth-Sun Pair:

Total starlight reflected from the planet		10^{16} watts
Reflected power per unit bandwidth:	£	10 watt/Hz
Total stellar radiated power per Hz at 10-cm	≈	10^6 watt/Hz
Human-produced nighttime light emission:	«	10^{12} watts
	«	10^{-3} watts/Hz
	«	10^{-4} reflected starlight
Human radio emission: Arecibo:	EIRP= $2.7 (10^{13})$	watts
	£	$2.7 (10^{13})$ watt/Hz
	≥	$3 (10^{12})$ reflected starlight
	≥	$3 (10^{16})$ human light emission
	≈	$3 (10^7)$ stellar flux density
Typical TV Transmitter:	EIRP= 10^6	watts/Hz (carrier)
	≥	10^5 reflected starlight
	»	10^9 human light emission
	≈	stellar flux density

Remote Sensing of Earth's Atmosphere

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Spectroscopic investigation of the minor and trace constituents of the atmosphere from the vantage point of near-Earth orbit can be made either by diffusely reflected sunlight, by transmitted solar radiation (i.e., by absorption during sunrise or sunset occultations), or by thermal emission. Each of these methods has its advantages and disadvantages. In the Earth orbit case the choice depends on a number of factors, including the required temporal and spatial coverage, and the extent of *a priori* knowledge of the physical and compositional structure of the atmosphere. Examples of the effect of these considerations on the performance of contemporary absorption and emission instruments are given. These include the Shuttle-borne, high resolution absorption measurements made over the past decade by the ATMOS instrument (0.01 cm^{-1} , 2 to 16 μm), the emission measurements of meteorology and atmospheric radiation instruments such as IRIS-D and HIS ($\delta\nu \approx 1 \text{ cm}^{-1}$, 4 to 15 μm) and the planned EOS 0.1 cm^{-1} emission instrument TES.

Two particular aspects of these methods are discussed: The first is the effect of spectral interference from the major infrared active gases (H_2O , CO_2 , CH_4 , N_2O) on the ability to detect and retrieve the abundances of anthropogenically significant trace constituents; the second concerns the effect of the thermal structure of the atmosphere on the appearance (or nonappearance) of features of candidate species (for example, CH_4) in emission spectra. Broadly speaking, the result of these considerations is that, for investigation of the detailed composition of the atmosphere, absorption measurements win hands down whereas, for spatial mapping of the more abundant species, measurements in the emission mode are more efficient.

However, in the case of observations of an unknown atmosphere, made from distances very large compared to the separation between the planet and its parent star, these factors are weighted quite differently. The competition may depend on the outcome of the technological challenge of making ultra high-precision amplitude measurements in the absorption case vs. achieving spectrally resolved discrimination of a very weak source in the other. Finally, an opinion will be offered on the required spectral resolution and S/N ratio, in the emission and absorption modes, for the identification of CO₂, H₂O, O₂, O₃, and CH₄ in an unknown planetary atmosphere at 10 ly distance.

Radiative Transfer and the Search for Extrasolar Life

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Radiative transfer has played and will continue to play a prominent role in the search for life outside of our solar system. Indeed, since the detection of the motion of photons in space is the primary method by which we infer the existence of extra solar systems, it would stand to reason that radiative transfer would also be instrumental in the detection of extrasolar life—similar to the remote sensing of life on Earth. Radiative transfer has its roots in the kinetic theory of gases as developed by Boltzmann at the end of the 19th century. The collision of particles with other particles and their subsequent motion between collisions, is one of the primary features described by kinetic theory. In addition, particles can be considered collectively in a statistical sense while still maintaining their invariant properties of motion. Radiative transfer is a special case of kinetic theory where photons do not interact with themselves. One of the basic elements of radiative transfer is the electromagnetic spectrum which determines the photon "particle" or "wave" nature. In this presentation, we treat the short wavelength end of the spectrum so photons are considered to be discrete packets of energy. Also of importance is how photons interact with the host medium. In particular, the law of deflection, commonly called the phase function, must be specified as well as the medium absorption properties. Radiative transfer has found application in analyzing stellar and planetary atmospheres, terrestrial satellite remote sensing to determine vegetation canopy reflectance and atmospheric corrections and weapons effects. The challenge of searching for extrasolar life will require both radiometric observation and radiative transfer modeling. The modeling issues concern the origins of the absorption features which appear as variations around a baseline in observed spectra. Here, we take a modeling approach in which we face our ignorance by taking advantage of natural averaging. A simple model for discussion purposes has been developed based on the 1-D, one-angle radiative transfer equation. A three region plane parallel medium, representing an atmosphere, vegetation and soil, is assumed with an isotropic /forward/backward scattering law. Results and some limited (common sense) conclusions concerning the detection of extrasolar vegetation are presented based on various scenarios of atmospheric composition and vegetation extent.

Habitable Zones Around Stars and Their Relationship to CO₂, O₂, and O₃ Abundances in Planetary Atmospheres

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The habitable zone (HZ) around a star is defined as the region in which an Earth-like planet could support liquid water. The continuously habitable zone (CHZ) represents the overlap of the HZs at two different instants in time. HZs move outward with time because main sequence stars get brighter as they age. The inner edge of the HZ is set by loss of water by way of photodissociation followed by escape of hydrogen to space. A conservative (i.e., pessimistic) estimate for the solar flux at which this phenomenon occurs is $1.1 S_0$, where S_0 is the present solar flux at Earth's orbit, 1370 W m^{-2} (ref. 1). The outer edge of the HZ is set by CO₂ condensation, which shuts off the stabilizing feedback provided by the carbonate-silicate cycle. Within the HZ, atmospheric CO₂ concentrations should increase with orbital distance as a consequence of this cycle. A conservative estimate for the solar flux at the outer edge of the HZ is $0.53 S_0$ (1). In terms of distance, the HZ for our own Solar System extends from at least 0.95 AU to 1.37 AU, and the 4.6-Gyr CHZ extends from at least 0.95 AU to 1.15 AU. Corresponding fluxes and distances for other types of stars are tabulated in ref. (1).

The reason that the HZ is important is two-fold: First, it indicates where inhabited planets might be found. And, second, it provides useful information about abiotic production of O₂. The only net abiotic source for O₂ is photodissociation of H₂O, followed by escape of hydrogen to space. The rate at which this occurs is governed by the mixing ratio of H₂O in the stratosphere, according to the principle of diffusion-limited flux (refs. 2 and 3). For Earth, the stratospheric H₂O mixing ratio is small (~ 4 ppmv), and the corresponding O₂ production rate is only $\sim 5 \times 10^7 \text{ O}_2 \text{ molecules cm}^{-2} \text{ s}^{-1}$. This is about 400 times smaller than the rate of O₂ production by photosynthesis followed by organic carbon burial (ref. 4) and about 100 times smaller than the rate of O₂ consumption by reaction with reduced volcanic gases (ref. 5). Thus, Earth's atmosphere would be virtually anoxic in the absence of life (refs. 3 and 6). A planet near or inside the inner edge of the HZ, however, could have a much higher stratospheric H₂O mixing ratio and a correspondingly larger abiotic O₂ source (ref. 1). Venus, for example, could have accumulated tens or even hundreds of bars of O₂ during the time that it lost its water (ref. 7). Thus, the identification of O₂ in a Venus-like planet's atmosphere would not necessarily indicate that life was present.

A second type of planet that could conceivably build up a high abiotic O₂ abundance would be one that was slightly larger than Mars, located beyond the outer edge of the HZ. The planet would need to be larger than Mars because Mars loses oxygen by dissociative recombination of O₂⁺ (ref. 8). So, Mars loses water to space rather than just hydrogen. Raising Mars' mass from $0.1 M_{\oplus}$ to $0.17 M_{\oplus}$ would be enough to shut off the loss of oxygen and allow O₂ to accumulate. But the planet could not be as large as Earth, because an Earth-sized planet would presumably emit reduced volcanic gases which would consume atmospheric O₂ as rapidly as it was produced (refs. 3 and 6). The planet would also need to be cold, like Mars, because a planet with liquid water on its surface would lose oxygen by rainout of oxidized gases, e.g., H₂SO₄, H₂O₂, followed by reaction of these species with reduced minerals in rocks (refs. 9 and 10). Further discussion of this issue can be found in refs. 11 and 12.

The practical way to search for life on extrasolar planets is to look for the 9.6- μm band of O_3 (ref. 13), which could be detected in nearby planetary systems with a space-based, infrared interferometer (ref. 14). O_3 is a sensitive indicator of atmospheric O_2 . The relationship between O_2 and O_3 concentrations in Earth's atmosphere has been studied by numerous investigators (e.g., refs. 15-17) and is reasonably well understood. Further work needs to be done to estimate the strength of the 9.6- μm band as a function of atmospheric O_2 level. Observations could presumably tell us where an extrasolar planet was located with respect to its primary's HZ, so we could determine whether the planet was Venus-like. Observations of other planets in the same system and their mutual interactions might allow us to derive planetary masses, so we could determine whether the planet in question might be Mars-like. If we could exclude both these possibilities, we could conclude that the planet was Earth-like and that the presence of substantial O_3 in its atmosphere was a strong indication of life.

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The Project DARWIN

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The search for life in the universe will be a central item in the scientific activity of the 21st century. The TOPS report states: "Much of religion and philosophy has focused on attempts to understand how we and our world came to be." We "ask about the prevalence of planetary systems throughout the universe (...) and the likelihood that other planets have given birth to life, even advanced and intelligent forms of lives. We live in a remarkable time, when human beings (...) have attained the possibility of finding the first real answers to some of these most meaningful questions."

We revisit the idea by R. Bracewell and R. Angel to detect exo-planets around nearby stars in the IR (6-17 μm) and analyze their spectra, searching for H_2O , CO_2 , CH_4 , NH_3 and O_3 spectral features. The presence/absence of CO_2 would be the indication of a deep similarity/difference with Solar telluric planet atmospheres. The presence of H_2O would indicate a habitable planet and O_3 reveal a large photosynthesis activity, indicating the presence of carbon chemistry based life. In agreement with these authors, we suggest a IR nulling interferometer pointing to the star and working as a coronagraph. Our main contribution is to propose an observatory made of 4 to 5 one meter class telescopes observing from 4 AU to avoid the Solar Zodiacal Light (ZL) background at 10 mm instead of eight meter ones observing from the Earth vicinity. This allows the mission to be feasible in the near future. The concept, named DARWIN, is under consideration by the European Space Agency for its Horizon 2000 Plus program.

Organic Reactivity Controls on Biogenic Gas Production, Oxidation, and Transport Processes

Christopher S. Martens, University of North Carolina at Chapel Hill

Biogenic methane is an important end-product of biogeochemical processes associated with the bacterial remineralization of labile organic matter. Organic matter remineralization in typical soils and sediments proceeds through a series of reactions in which the available oxidant that yields the greatest free energy determines the dominant process at a particular horizon. If O_2 is present, aerobic decomposition is the major pathway. Upon depletion of dissolved O_2 , organic matter degradation shifts to nitrate reduction. Once nitrate is fully utilized, metal oxides (MnO_2 and Fe_2O_3) serve as oxidants. When metal oxides are no longer available, organic matter remineralization proceeds through sulfate reduction. The final reaction in the series, methane production, generally occurs after the sulfate pool has been exhausted. In sediments prone to gas production, sulfate reduction and methane production are likely to be the dominant decomposition reactions due to limited supply of other oxidants.

The occurrence of methane production and other decomposition reactions in soils and sediments is ultimately controlled by the flux of reactive organic matter. However, the rates, and thus depth distribution, of these reactions vary dramatically in response to seasonal variations in temperature. Following its production, the distribution of methane in sediments is further modified by

consumption (oxidation) and transport processes which may also exhibit pronounced seasonality in their absolute rates and relative importance. The production and transport of dissolved and gas bubble methane from organic-rich sediments can be predicted by simple mass conservation models in which reaction rates are balanced by diffusive and advective transport. Reactive organic matter input rates, concentrations of sulfate and other oxidants, temperature, transport mechanisms, and pressure exert primary control on resulting fluxes and distributions.

Biogenic methane is generally distinguished from thermally generated gas through its relatively depleted stable carbon isotopic composition as well as >1000-fold higher concentration than other light hydrocarbons. However, time-course incubation experiments at room temperature with natural sediments reveal a large range in isotopic composition of bacterially produced methane which overlaps values for thermally-produced methane found in hydrothermal environments. Heating of organic matter in hydrothermal sediments generates relatively C-13-enriched methane and C-1/C-2+C-3 light hydrocarbon ratios less than 100. Large quantities of short chain organic acids such as acetate which may serve as microbial substrates are also generated during such thermal alteration. We have much to learn about microbial versus thermal controls on the concentrations and isotopic composition of light hydrocarbons during their production and oxidation.

Exobiology: Laying the Groundwork in a Search for Extrasolar Life

Michael Meyer, Exobiology Program, NASA Headquarters

How did life begin, both here and perhaps elsewhere? Are we alone, a chemical fluke, or are we the result of a process common in the universe? Prior to this century the question of our origin has been relatively unconstrained. With knowledge gained through experimentation and space science—about Earth, the solar system, and the universe—the question of our origins has become a serious scientific quest.

Exobiology, the study of the origin, evolution, and distribution of life in the universe, embodies this quest. With the recognition that: chemical evolution proceeded rapidly to life on Earth, life may be a natural consequence of planetary evolution, and planetary systems may be common in the universe, life is likely to be common in the universe. How can we find it?

With modeling, observation, and sampling in our solar system, we can learn of the planets' evolution through time. What is the relative importance of distance from the sun, bulk composition, and mass that determine whether the planetary body could have ever sustained life. What planetary bodies are the better candidates for life around other stars?

What are the potential signatures for life? So far, we have only one example, rather evolved life at that. How would Earth's biosphere appear from space? Technology has an obvious signature but technology has been here for an extremely limited period of time. For the last 2 billion years, Earth's biosphere has been dominated by oxygenic photosynthesis—ozone would be an indicator. Chemical disequilibria are maintained by biology and could be indicative of life, for example methane or nitrous oxide in the presence of oxygen. But what of early Earth? What combination of reduced

species would be indicative of life in a reducing atmosphere? Perhaps Earth's atmosphere was dominated by volcanic activity during its first 1.5 billion years, swamping any biological signature. An alternative maybe to search for a predominance of an optically active pigment, like chlorophyll or rhodopsin.

Exobiology can contribute to the search for life elsewhere by broadening our understanding of the origin and evolution of life. Specific questions that could be addressed are: What planetary characteristics would indicate habitability? What planetary characteristics would be most diagnostic of life? and at what stage? What planetary characteristics would be most detectable?

Reduced Biogenic Carbon Gases: Who Cut the Cheese?

Ronald S. Oremland, U.S. Geological Survey

The Earth's biosphere represents the major source for important constituents of its current atmosphere including N_2 , O_2 , CH_4 , dimethylsulfide (DMS), and certain halocarbons. Reactive species derived from an O_2 -rich atmosphere (i.e., hydroxyl radicals) destroy reduced carbon gases in the troposphere thereby constraining both their abundance and residence times. Methane, the most abundant hydrocarbon, has a mixing ratio of ~ 1.7 ppm and a residence time of ~ 8 years. However, the biosphere has existed for over 3.5×10^9 years, for much of which overall anaerobic conditions prevailed. Because of the ancient divergence of the 3 main biological kingdoms, it is likely that the Archaea, as represented by methanogens, have been present for all of the time the Earth's biosphere has been in existence. Because of the absence of oxidizing species in the Archaen troposphere (i.e., OH) and the lack of chemical oxidants available to bacteria for the destruction of CH_4 (e.g., SO_4 , Fe^{3+}), it is reasonable to assume that methane mixing ratios were much higher than present levels, possibly by orders of magnitude. A corollary of this line of reasoning is that volatile precursor substrates of methanogens, such as DMS, methane thiol, methylated amines, methanol, hydrogen, acetic and formic acids may also have been more abundant. Other gases of biogenic origin which could have entered into methanogenic pathways by nucleophilic exchange reactions would include halocarbons like methyl bromide.

A CH_4 -rich Archaen atmosphere would also have significant acetylene present as a consequence of a complex series of photocatalytic reactions. *Pelobacter acetylenicus* is an anaerobe which grows on acetylene by first hydrating it to form acetaldehyde and then dismutating this intermediate to form ethanol and acetate. The formation of ethanol and acetate would have provided a uniform source of carbon and energy around which Proterozoic microbial communities could have developed. The appearance of oxidants like SO_4^- , S^0 , and Fe^{3+} as conditions became less reducing would have created niches for organisms capable of oxidizing acetate and ethanol to CO_2 . This acetylene-based food chain has implications for the possibility for life on planets with Jovian-like atmospheres.

The difficulty for unequivocal detection of life on planets harboring microbial ecosystems analogous to this concept of an anoxic Archaen would be the discovery of "false positives." Methane, higher hydrocarbons, and many other simple organic compounds are abundant in the outer planets, comets and other heavenly bodies. The detection of other methylated compounds in addition to CH_4 , such as

DMS, methylhalides, and methylated amines, could provide supplemental data which would strengthen the case for the presence of microbial life on anoxic, extra-solar planets.

Multiple Blue Dots

Tobias Owen, University of Hawaii

In our solar system, there are two blue dots: Earth and Neptune. This leads to the question - suppose an early Earth-like planet has a methane-dominated atmosphere. How could you tell such a planet from a Neptune, or a Titan? The first approach is simply to use celestial mechanics to give the mass and stellar separation of the objects in question. Large mass tells you it's a giant. Large separation tells you it's probably too cold, but spectroscopy can give you the temperature and prove it. Is that true? Not always. Spectroscopy can also identify abundant H_2 in a planet's atmosphere, again proving it's a giant. What about Titan? IR observations alone don't give you the surface temperature. Hence you can't rule out an intense atmospheric greenhouse effect that could raise the surface temperature into the liquid ammonia-water range even at large separation of object and star. Such models existed for Titan before radio wavelength observations showed the surface was very cold, hence atmosphere was thinner than those models required (and did not contain NH_3).

Remote Sensing of the Earth's Biosphere

David L. Peterson, NASA Ames Research Center

Remote sensing in the optical spectrum of the biosphere takes advantage of the same atmospheric transmission windows that life itself has so successfully exploited. By measuring the radiation exiting the top of the atmosphere and accounting for the scattering and absorption characteristics of the atmosphere, we are left with the reflected radiance of the surface (land and oceans) where clouds and their shadows do not obscure the view. Scattering and absorption by the surface, as well as topographic illumination differences, modify the radiation. For vegetation, the reflectance is first altered by cellular and molecular processes. Waxes produce specular reflectance, cell walls produce diffuse scattering, and cell contents produce absorption. A similar process occurs in water by microorganisms such as phytoplankton. Reflectance of whole canopies cannot be explained by leaf properties alone; multiple scattering, shadows, soil signatures and other objects also contribute. The first optical instruments were optimized to measure the strong contrast in vegetation between IR and visible, giving rise to time series of global maps related to capacity to absorb visible light for photosynthesis. Spectroscopic observations have never been available from space, but offer new opportunities for analysis. For plants, a look at their biochemical properties at a regional scale is possible. For oceans, various absorption pigments and organisms can be observed, especially important for highly productive coastal waters. An innovation Ames is working on is imaging interferometry, an instrument to measure the spectral continuum with high signal to noise at low cost, size and weight. Outside the optical, thermal and microwave observations have also been

developed that mainly, in the latter case, measure macroscopic characteristics of vegetation, structure that organizes water in various forms.

Biogenic Trace Gases on Earth: Understanding the Controls on Global Sources and Sinks

Christopher S. Potter, NASA Ames Research Center

There is little doubt that life on Earth, including human life, has a significant impact on the contemporary composition of the planet's atmosphere. All the major "greenhouse" trace gases, CO₂, CH₄, N₂O, O₃, have important interactions with biospheric processes that vary in a fairly predictable manner, both seasonally and inter-annually. Our general understanding of the physical and chemical controls over global biosphere-atmosphere exchange of trace gases has increased dramatically over the past several years, owing in part to advances in the coupling of remote sensing technology and simulation modeling of ecosystem processes. We can now develop reliable global images that characterize optimal physical conditions for major life forms on Earth and their associated exchange of biogenic trace gases with the atmosphere. For example, using computer models developed at NASA Ames we have deduced that production of oxygen by terrestrial plant-life appears to optimize over a fairly narrow range of 5-35° C, whereas production of CO₂ by soil microbes is severely limited by rainfall rates less than about 2 cm per month. Although characterization of optimal conditions for planet-wide colonization by Earth-like species may prove useful for identification of favorable conditions (habitable zones) for life on distant bodies, numerous questions remain as to whether even a globally significant pattern of biosphere-atmosphere exchange of trace gases will be detectable over great distances. Can a potential seasonal pattern of biogenic gas exchange be separated from other sources of signal variation in multi-temporal observations of distant planets? Can hemispheric or continental differences in gas dynamics be resolved with near-term technology? If such discrimination becomes feasible, what unique combination(s) of trace gas cycles should we be searching for, in order to characterize life as we know it? Recent advances in remote sensing Earth observations should soon provide answers to at least the third question posed here.

Contrasts in the Earth's Present and Early Methane Budget

William S. Reeburgh, University of California, Irvine

Concern regarding the climate consequences of recent increases in the atmospheric CH₄ mixing ratio has focused research on the Earth's present-day atmospheric CH₄ budget. The Earth's CH₄ budget is based on constraints involving the atmospheric burden, residence times, and isotope composition of atmospheric CH₄. The atmospheric CH₄ budget (actually a net emission budget nearly balanced by photochemical oxidation) provides no information on processes that consume CH₄ before emission to the atmosphere. Predicting changes in source and sink terms under different conditions requires a focus on the gross global CH₄ budget. Global gross production of CH₄ is the quantity of CH₄

entering the atmosphere (net emission) plus global CH₄ oxidation (photochemical and microbial); it has been estimated by adding estimated and measured oxidation to each of the budget source terms.

There appears to be no way to directly estimate the early Earth's atmospheric CH₄ mixing ratio, but the young Earth's CH₄ budget can be approached by adjusting source and sink terms to conditions estimated to exist then. Early Earth CH₄ sources are expected to be fewer and smaller than present-day sources. Photosynthetic primary production was likely smaller than present and occurred in bacterial mats bathed in shallow fresh and saline waters. Terrestrial primary production by vascular plants was absent, so the large wetland and rice production source terms for CH₄ were missing. Source terms involving anthropogenic activities (landfills, enteric fermentation, gas and oil production) were also absent. Provided sufficient organic matter was present, the tectonic processes that appear to lead to present-day CH₄ clathrate formation may have been active.

The major present-day CH₄ sink, photochemical oxidation by the OH radical, was apparently active in a low-oxygen atmosphere. Wayne suggests that atmospheric lifetimes were about 5-fold longer than the present-day lifetime of 10 y. Carbon isotope evidence suggests widespread methanotrophy during early Earth history. Studies of methanotroph physiology may place bounds on the CH₄ concentration in some early Earth environments, but not necessarily the atmosphere. Methanogenesis and methanotrophy are closely coupled and consume a major fraction (~50%) of the CH₄ produced before emission to the atmosphere. Microbially-mediated CH₄ oxidation reactions on the young Earth could have been similar to those observed under present-day conditions. However, under the low-oxygen and low-sulfate conditions presumed for the young Earth, they may have been a less effective barrier to CH₄ emission.

How Definitive Would Detection of H₂O, CO₂, O₂/O₃ and CH₄/O₂ be for the Identification of Life on Planets of Other Stars?

Carl Sagan, Cornell University

In its December 1990 flyby of Earth, the Galileo spacecraft found evidence of abundant gaseous oxygen, a widely distributed surface pigment with a sharp absorption edge in the red part of the visible spectrum, and atmospheric methane in extreme thermodynamic disequilibrium; together, these are strongly suggestive of life on Earth. Moreover, the presence of narrowband, pulsed, amplitude-modulated radio transmission seems uniquely attributable to intelligence. These observations constitute a control experiment for the search for extraterrestrial life by modern interplanetary spacecraft—as well as an indication of which types of observations may be fruitful in the search for life on planets of other stars. But mere detection of H₂O and CO₂ — or even O₂/O₃ — in the atmosphere of a terrestrial planet is insufficient evidence of life: Nonbiological photolytic processes can—depending on atmospheric structure and oxidation state of the crust—generate significant quantities of O₂.

Life Detection by Atmospheric Analysis: Avoiding the Geocentric Bias

Andrew Watson, University of East Anglia

Much discussion has focused on the use of ozone as a diagnostic for life in a planetary atmosphere. While it is true that, of the terrestrial planetary atmospheres in this solar system, Earth has the most ozone and this is due to the presence of life, it would be a mistake to believe that detection of ozone will necessarily equate to detection of life.

Is an oxidizing atmosphere on a terrestrial planet a necessary condition for there to be life on its surface? Clearly not, because there was life on Earth long before there was an oxidizing atmosphere.

Is an oxidizing atmosphere then, a sufficient condition to diagnose life at a planet's surface? It would be sufficient only if there is no inorganic process which can give rise to such an atmosphere. However, hydrogen escape could do exactly that: A planet similar to the Earth but somewhat closer to the sun, so that sufficient solar flux was absorbed to generate, a runaway or moist greenhouse would be subject to substantial hydrogen escape, leading to progressive oxidation of the surface environment. How much free oxygen could be generated in the atmosphere would depend on, for example, the rapidity of tectonic/volcanic activity at the surface, but we cannot rule out the small amounts of oxygen needed to generate ozone.

Granted that oxygen is neither necessary nor sufficient to diagnose life, Is it nevertheless inevitable that life on a planet will drive the atmosphere towards oxidation, so that given enough time, a biosphere will come to live under an oxidizing atmosphere?

I'd argue that it is not inevitable, and that an alternative evolution would result in the environment becoming more and more reducing. However, it is true that the environment would be unlikely to stay in the same overall oxidation state as it would be without life; it would become either more strongly reducing or more strongly oxidizing. Of these the second is more energetically favorable, so might be expected if initially both CO_2 and CH_4 were present. This follows from a consideration of possible schemes of photosynthesis/respiration which would allow an energetic biota to arise.

All of the above suggests that a program to detect life on extrasolar planets should not concentrate exclusively on detecting ozone, but should explore the possibilities of detecting as many other volatiles as possible. With a few exceptions, life on Earth produces all of the volatiles which can be made from the elements C, N, H, S, O, Cl, and Br. Huge amounts of energy go into the production of gases such as CH_4 , N_2O , $(\text{CH}_3)_2\text{S}$. As Lovelock pointed out, it is not the presence or absence of any one gas, but the degree of disequilibrium in the mixture, which gives the clue to the presence of life. We therefore should explore what spectroscopic signals should be expected from possible mixtures of such gases, for we will need to detect at least one oxidized and one reduced gas to have any real confidence that we have a "life-like" atmosphere.

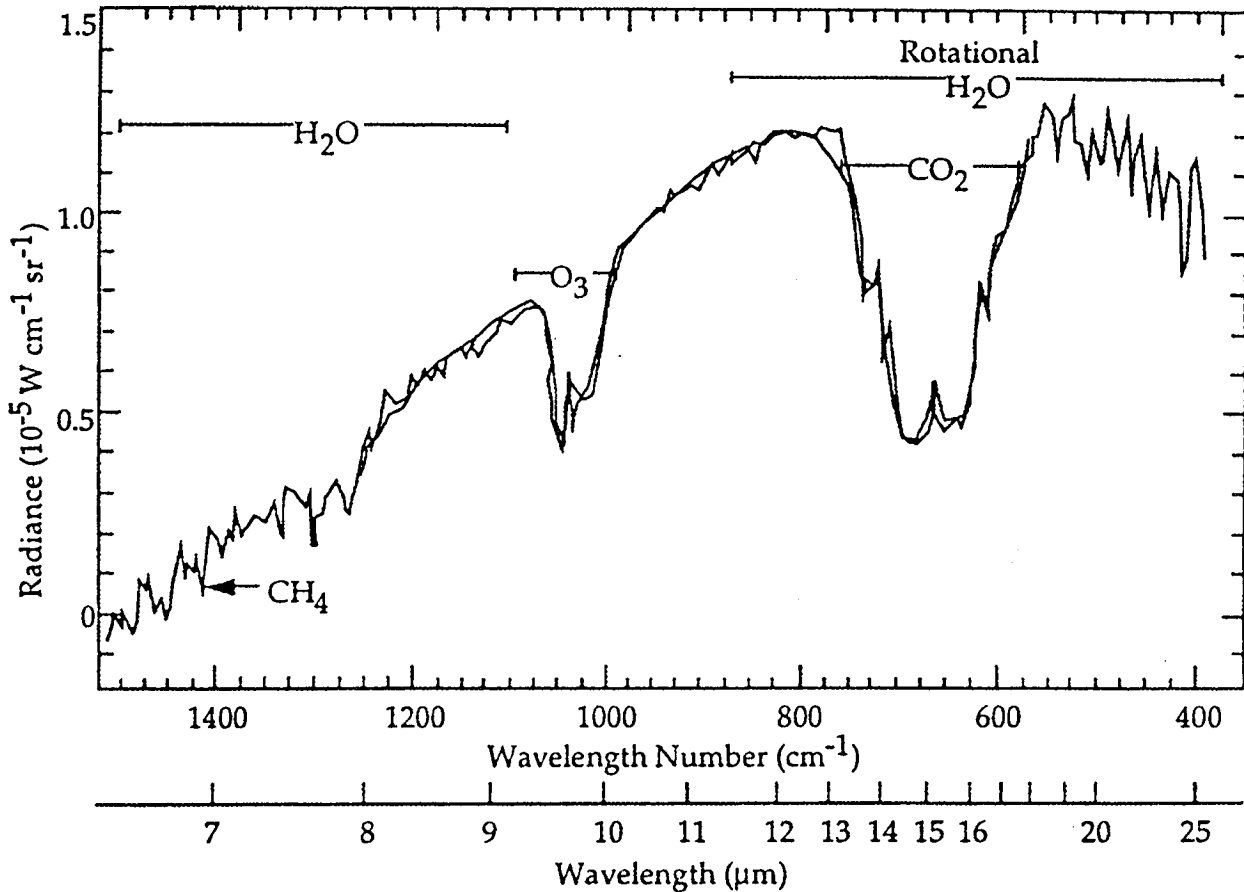


Figure 4. The infrared spectrum of the Earth, as observed from an orbiting Nimbus satellite, shows a variety of spectral features (from "A Road Map for the Exploration of Neighboring Planetary Systems," C.A. Beichman, ed., JPL Publication 96-22, 1996).

A Space-Based, Imaging, Nulling Interferometer: What Can It See?

Nick Woolf and Roger Angel, Steward Observatory, University of Arizona

Planet finder interferometers "DARWIN" and "OASES" have been described by Léger, et al., (Icarus in press) and by Angel and Woolf (Astrophysical Journal submitted). Although these devices have some differences, they also have features in common. There are four (or five) mirrors of 1m diameter. The devices are about 50m across, and have an angular resolution of about 0.03 arc seconds. They can observe and take spectra of Earth-like planets out to a distance of about 10pc, in the 7-17 m region and they are just sensitive enough to detect water, carbon dioxide and ozone in an Earth-like planet.

The specific needs in making these minimal finding and spectroscopic observations are:

- 1) The starlight is interferometrically nulled so as to be no more than the signal from a single planet.

- 2) The telescopes and all components in the optical path are radiatively cooled to a temperature where their thermal emission is negligible.
- 3) The devices operate at about 5AU from the Sun, where the thermal emission of our own system's zodiacal dust is negligible.
- 4) The detected noise is the photon shot noise of the zodiacal dust of the external system.
- 5) Signals are very feeble and so detectors of exceptionally low noise are needed.
- 6) The signals from all planets are multiplexed by the interferometer, so that all planets of a system are observed simultaneously. Reconstruction produces a 3-dimensional result with two-dimensional maps of the system (which shows the planets revolving around their star), and the third dimension shows intensity against wavelength for each source, i.e., it is the spectrum with a spectral resolution built into the device.
- 7) The spectral observations take a long time to observe (weeks to months per system) to achieve adequate signal/noise.
- 8) The technological requirements to make these observations are harder to meet than they have been for any spacecraft to date. There are very tight tolerances for pointing, phasing and amplitude control that require new techniques to be developed. And all systems must operate where no human help can be made available.

Seeing further, and the exo-zodiacal dust limit

The limitations of the system are first, that an "Earth" has a standard luminosity, and so can only be seen out to a standard distance. Secondly, the device has a limited angular resolution. If the planet is too close to the star, it cannot be resolved. A system with 1m mirrors is just sensitive enough to see "Earths" out to 10pc. If the zodiacal dust of other systems has more emission than our solar system, then the sensitivity drops. If there is four times as much dust emission, then we can only see out half as far, to 5pc. To bring back sensitivity, we can increase the size of the telescopes, two-meter mirrors can see twice as far as one-meter mirrors.

For the second limitation, an interferometer with doubled linear dimensions has double the angular resolution. A ~50m device can resolve an "Earth" around a "Sun" at 10pc. Intrinsically fainter stars will have their "Earth" closer in, and so require higher angular resolution. A 100 meter interferometer can resolve an "Earth" around a "Sun" out to 20pc.

Seeing CH₄ and N₂O

Methane would be meaningful to observe because it is indicative of the anaerobic decay of organic matter. Nitrous oxide is produced on Earth by the Nitrogen cycle, and as such indicates an atmosphere of oxygen and nitrogen, the fixing of nitrogen, presumably by life processes, and oxidation of ammonia to N₂O. Bands of methane and nitrous oxide, most visible near 7.8m and 8.6m respectively are harder to see than ozone for two reasons. First they are narrow, and secondly

methane occurs at the short wavelength end of the spectral band where an Earth-temperature planet has a reduced flux (also water absorbs there). The attached spectrum of part of Earth, from the Nimbus satellite, show bands about 10 times narrower than Ozone. (The individual lines have a width of about 0.002m). The methane has a comparable central intensity, but the nitrous oxide is much weaker. The spectral resolution to see them has to be about 0.05m. Also, the flux at the Methane band is reduced by about 2.5 compared with Ozone. For Methane we are trying to detect a roughly 25 times smaller amount of light removed from a planet spectrum, and this requires about 25 times larger collecting areas to achieve the same detectability as Ozone. This would require the 1-meter telescopes to be replaced by a set of four 5-meter class telescopes. If 1.5-meter telescopes were considered for a "Mark I" planet finder, then 7.5-meter class telescopes are needed for "Mark II". For N₂O the band is about 5 times more shallow, and would need about 250 times the collecting area, or about 15m apertures.

Simple substitution of larger round mirrors in a planet finder would not be enough, because the angular resolution of the mirrors would cut out signals from outer planets. A preferred scheme would have rectangular mirrors, preferably of about 2x10 m. This would be fine for methane. Nitrous Oxide needs a different solution. To observe Methane, it would be very helpful for design studies of a Next Generation Space Telescope to be coordinated with planet finder studies. A form of NGST in which the aperture is elongated would be helpful for fitting into a planet finder, and this option is being considered by the NGST designers.

Detection of molecular Oxygen

Molecular oxygen does not have strong bands in the 7-17 m spectral region. It seems likely that the optimum wavelength for detection is the A band at the long wavelength (red) end of the visible spectrum. At those wavelengths, photon fluxes are about 20 times less than in the 7-17 m region. Also, the A band is relatively narrow (D/I) compared with the breadth of the IR ozone band. Thus about 200 times as much collecting area will be needed to see it as to see Ozone—all else being equal. A roughly 15-20m class space telescope is needed.

Observing a planet with a large telescope in this region has been discussed by Sandler and Stahl. In their simulations of a 6 meter aperture, the planet image sits on a pedestal of light from the central star, which is 1000 times brighter than the planet. A 15-20m telescope would have a sharper diffraction pattern, and the planet/"background" signal would be rather similar to that for a planet finder mission. Detailed simulation it is needed to determine the minimal telescope size, but reduction much below 15m seems unlikely.

None of the spectroscopic observations discussed above is remotely as difficult as the simplest imaging of an external planet's surface. The optimum study to follow the first spectroscopic observations of external planets is—more spectroscopy. An optimum sequence would seem to be, first a planet finder with small mirrors, then a planet finder with large mirrors, then a third generation Space Telescope. The benefit is that it should be possible to start exploring those cyclic processes which are chemical indicators of life on Earth.

Disequilibrium Chemistry by Impacts

Kevin Zahnle, NASA Ames Research Center

The fragments of comet Shoemaker-Levy 9 struck Jupiter in July 1994. Each impact produced strong shocks both at the impact site and again when the ejecta plume fell back on the atmosphere. The resulting chemistry was distinctive. Reported products ranged from mildly oxidized (H_2O) to neutral (CO , S_2 , OCS) to reduced (CS , CS_2 , HCN , C_2H_4). The impacts also produced a great deal of dust, in part silicate (mildly oxidized) and in part carbonaceous (reduced). Evidently the impacts sampled several kinds of gas. Some gases were jovian, very dry to begin with, and by shock chemistry converted to HCN , perhaps CS and CS_2 (if H_2S were present), and tholins and/or soot (both words used in broad sense). Other parcels were derived more from comets. These supplied the water and the oxygen for CO , and were probably the source of sulfur for S_2 . But apparently there were no very strongly oxidized parcels, which would have produced the unobserved compounds SO , SO_2 , and CO_2 .

Reentry gas temperatures were directly measured via hot CO . Gas temperatures rose quadratically with time, reaching 5000 K towards the end of the event. The dust was much cooler, roughly 600 K, and dust temperatures were sensibly constant over the ten minutes of strong IR radiation. Such temperatures are nearly ideal for surface-catalyzed chemistry, especially for the Fischer-Tropsch reactions that convert CO to hydrocarbons.

Although chemistry on Jupiter does not directly relate to chemistries of early Earth, it is clear that atmospheric chemistry of imaginary terrestrial planets could be greatly perturbed by impacts. Shocks at the impact site, shocks as ejecta reenter the atmosphere, and catalytic action by warm grains all offer means by which an atmosphere could be put into transient thermochemically disequibrated states resembling somewhat the chemistry of relatively high temperatures. Very big impacts would process the whole atmosphere. It may take a long time to return to the "steady state."

To first approximation, one expects to thermally process some 10 impactor masses of air in an impact. An event on the scale of that made the lunar Orientale impact basin could process a 1 bar atmosphere. Under favorable conditions, as might be produced by a relatively reduced impactor, one might expect unexpected species (e.g., CH_4 , say) at the percent level, which would then take thousands or perhaps even millions of years of atmospheric photochemistry to remove. Earth received hundreds of impacts on this scale in the hundreds of millions of years before 3.8 Ga; thus it is possible that a fair fraction of Earth's youth was spent in impact-perturbed states rather than in geochemically and photochemically mediated steady states. Thus otherwise similar young planets may exhibit a wide range of early atmospheres, any of which might have characterized Earth at a particular moment in time, and some of which would seem especially conducive to the origin of life.

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