Synthetic Spectra of Simulated Terrestrial Atmospheres Containing Possible Biomarker Gases

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NASA's proposed Terrestrial Planet Finder, a space-based interferometer, will eventually allow spectroscopic analyses of the atmospheres of extrasolar planets. Such analyses would provide information about the existence of life on these planets. One strategy in the search for life is to look for evidence of O_3 (and hence O_2) in a planet's atmosphere; another is to look for gases that might be present in an atmosphere analogous to that of the inhabited early Earth. In order to investigate these possibilities, we have calculated synthetic spectra for several hypothetical terrestrial-type atmospheres. The model atmospheres represent four different scenarios. The first two, representing inhabited terrestrial planets, are an Earth-like atmosphere containing variable amounts of oxygen and an early Earth-type atmosphere containing methane. In addition, two cases representing Mars-like and early Venus-like atmospheres were evaluated, to provide possible "false positive" spectra. The calculated spectra suggest that ozone could be detected by an instrument like Terrestrial Planet Finder if the O_2 concentration in the planet's atmosphere is ≥ 200 ppm, or 10^{-3} times the present atmospheric level. Methane should be observable on an early-Earth type planet if it is present in concentrations of 100 ppm or more. Methane has both biogenic and abiogenic sources, but concentrations exceeding 1000 ppm, or 0.1% by volume, would be difficult to produce from abiogenic sources alone. High methane concentrations in a planet's atmosphere are therefore another potential indicator for extraterrestrial life. © 2000 Academic Press

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INTRODUCTION

The steady growth in the number of giant extrasolar planets detected since 1995 (Marcy and Butler 1998) has bolstered interest in two questions: How many terrestrial-type planets might exist in other solar systems? And do any of these Earth-like planets harbor life? Unfortunately, the methods currently used to detect extrasolar planets are inadequate to answer these questions. Radial velocity measurements are not sensitive enough to detect a planet of Earth's mass, and the extreme disparity in brightness between an average star and its planetary companions makes direct observation of the companion by ground-based telescopes impossible. Such measurements could be made, however, by NASA's proposed Terrestrial Planet Finder (TPF) mission (http://tpf.jpl.nasa.gov), which would utilize a space-borne interferometer to null out the overpowering light of a planet's parent star. TPF's observations would be made in the thermal infrared, where the emission from an Earth-like planet would be at a maximum (Angel and Woolf 1996). This method could potentially allow observation of the spectrum of a planet's atmosphere at distances as far as 15 pc from our Solar System, according to current baseline instrument plans (four 3.5-m, free-flying telescopes with a 50–1000 m baseline, orbiting at 1 AU). A boom-mounted configuration might also be used. Studies are underway to determine the relative merits of the two different approaches.

What can observation of the spectrum of a planet's atmosphere tell us about the existence of life on the planet? In 1965, Joshua Lederberg suggested a possible criterion for detecting life on a planet's surface: atmospheres that had been modified by biota should exhibit marked departure from thermodynamic equilibrium (Lederberg 1965). This criterion would be necessary, but not sufficient, to demonstrate the existence of life, as any atmosphere will display some degree of disequilibrium as a result of the competition between thermally and photochemically induced reactions. However, an extreme degree of disequilibrium would be quite suggestive of life. Lovelock (1965) elaborated on these ideas later in the same year, noting that a signature of life on Earth is the simultaneous presence of highly reduced gases such as CH_4 and N_2O, along with the oxidized gas O_2. All of these gases are produced predominantly by biological activity. Sagan *et al.* (1993) used data from the Near Earth Mapping Spectrometer (NIMS) on the *Galileo* spacecraft to show that

all three of these gases could be detected on Earth from space, so that one could in principle ascertain that Earth is inhabited without visiting its surface.

Although remote spectroscopic detection of life appears possible, we are limited in the types of observations we can make by the inherent difficulty in viewing terrestrial-type planets in other planetary systems. In particular, the thermal IR region of the spectrum that TPF will observe will not allow the direct observation of N_2O or O_2. Although N_2O has absorption lines in this region, the absorption is rather weak for a planet like Earth because N_2O is present only in small concentrations (0.3 ppm) and is mostly confined to the troposphere. O_2 does not absorb radiation in the thermal IR. Other interesting gases do absorb strongly in this range, however, including CO_2, H_2O, O_3, NH_3, and CH_4. CO_2 and H_2O both appear to be essential for the existence of life, but do not by themselves imply that life exists. Ammonia is produced by the processes of life on Earth, but is present only in small and highly variable amounts (0.1 to 10 ppb) in Earth's atmosphere, as it rapidly photolyzes. Even in a reducing, primitive atmosphere, the expected amount of ammonia would be small; the model of Brown (1999) indicates that an ammonia surface flux of 10^9 cm^{-2} s^{-1} could sustain a mixing ratio of only 10^{-10} because of rapid photolysis. This flux is ~10 times the current flux of ammonia from anthropogenic and naturally occurring biotic sources (Brown 1999). Thus, it seems unlikely that ammonia would be observable in a terrestrial-type atmosphere by an instrument like TPF. Similarly, N_2O photolyzes rapidly in low-O_2 atmospheres and is not expected to have been abundant on the early Earth (Kasting and Donahue 1980). The biotic trace species OCS and CS_2 might be suggested as useful biomarkers; however, they both photolyze in the near-UV (Okabe 1978) and hence could not be expected to accumulate in an Earth-like atmosphere to a level measurable by a TPF-class interferometer. By contrast, CH_4 photolyzes only at very short wavelengths ($\lambda < 1450$ Å) and can therefore have a long photochemical lifetime in a weakly reduced, primitive atmosphere. Hence, O_3 (in modern Earth-analogue atmospheres) and CH_4 (in early Earth-analogue atmospheres) appear to be the best gases to look for as indicators of extraterrestrial life.

At this point the case could legitimately be made that our search strategy is somewhat chauvinistic, as we are considering gases that are the result of an Earth-based biology. Unfortunately, this situation is borne of necessity. The question of what gases a more "alien" biological activity might produce must wait until plausible alternative biologies are postulated. (This may be a long wait!) In the meantime, the general characteristics discussed above must suffice to guide our investigation, as we only know of one case on which to base our search.

OZONE AS A POSSIBLE INDICATOR OF LIFE

Angel *et al.* (1986) first pointed out the significance of ozone as a potential biomarker. As shown in Fig. 1, ozone has a strong absorption feature at 9.6 μm, in the middle of TPF's planned observing range. Ozone also has a nonlinear dependence on the atmospheric O_2 abundance, rising to appreciable concentrations even at relatively low O_2 levels (Ratner and Walker 1972, Levine *et al.* 1979, Kasting and Donahue 1980, Kasting *et al.* 1985), and is therefore in some ways a more sensitive indicator of O_2 than O_2 itself. The only significant abiotic net source of O_2 in the Earth's atmosphere is the photolysis of water in the stratosphere followed by the escape of hydrogen to space (Walker 1977), which presently yields a production rate of approximately 4×10^7 O_2 molecules cm^{-2} s^{-1}. The rate of abiotic O_2 production on early Earth should have been even smaller, as the stratosphere would probably have been cooler and dryer than it is today (Kasting and Ackerman 1986).

The major sinks for O_2 are the oxidation of Earth's crust and reaction with reduced volcanic gases such as CO and H_2. Holland (1978, pp. 291–292) estimates the present outgassing rates of H_2 and CO to be 11 and 3×10^{11} mol/yr, respectively. This gives a total volcanic oxygen sink of 1.4×10^{16} mol/yr, or 5×10^9 molecules cm^{-2} s^{-1}. Thus, this sink alone overwhelms the abiotic oxygen source by a factor of 60 or more. Models of Earth's early atmosphere based on these numbers indicate that O_2 mixing ratios should have risen to only 10^{-4} and 10^{-3} in the stratosphere, and ~10^{-13} at the surface in the absence of a biotic source (Kasting *et al.* 1979, Pinto *et al.* 1980). However, even in the absence of volcanic activity, the existence of liquid water on the surface of the planet should facilitate the oxidation of the planet's crust, creating a large O_2 sink. Thus, for planets positioned within the liquid water region, or habitable zone, of a star, the simultaneous presence of the signatures of O_3 and water in the planet's spectrum would imply a large source of O_2. This source would best be accounted for by the existence of life on the surface.

SYNTHETIC SPECTRA OF O_2-RICH ATMOSPHERES

In order to determine the lower limits of oxygen abundance to which TPF is sensitive, a series of synthetic spectra of atmospheres containing varying amounts of oxygen were created. The ozone profiles, from the model of Kasting *et al.* (1985), are shown in Fig. 2. The tool used to generate these spectra was the Line-By-Line Radiative Transfer Model (LBLRTM) developed by Clough *et al.* (1992), with line parameters provided by the HITRAN 92 database. The accuracy of the code can be demonstrated by comparing a synthetic spectrum of the outgoing IR radiation from the Earth produced by LBLRTM with the spectrum obtained by the IR spectrometer aboard the *Nimbus 7* satellite (Fig. 1).

The atmosphere was modeled up to a height of 60 km, using 30 2-km thick layers. Our viewpoint was from space, looking down at a zenith angle of 60°. This angle was chosen because we assume that the instrument will be viewing the planet with one-pixel resolution, so the appropriate viewing angle is the average over a sphere. Spectra were computed between the wavenumbers of 400 and 1600 cm^{-1}. While the resolving power

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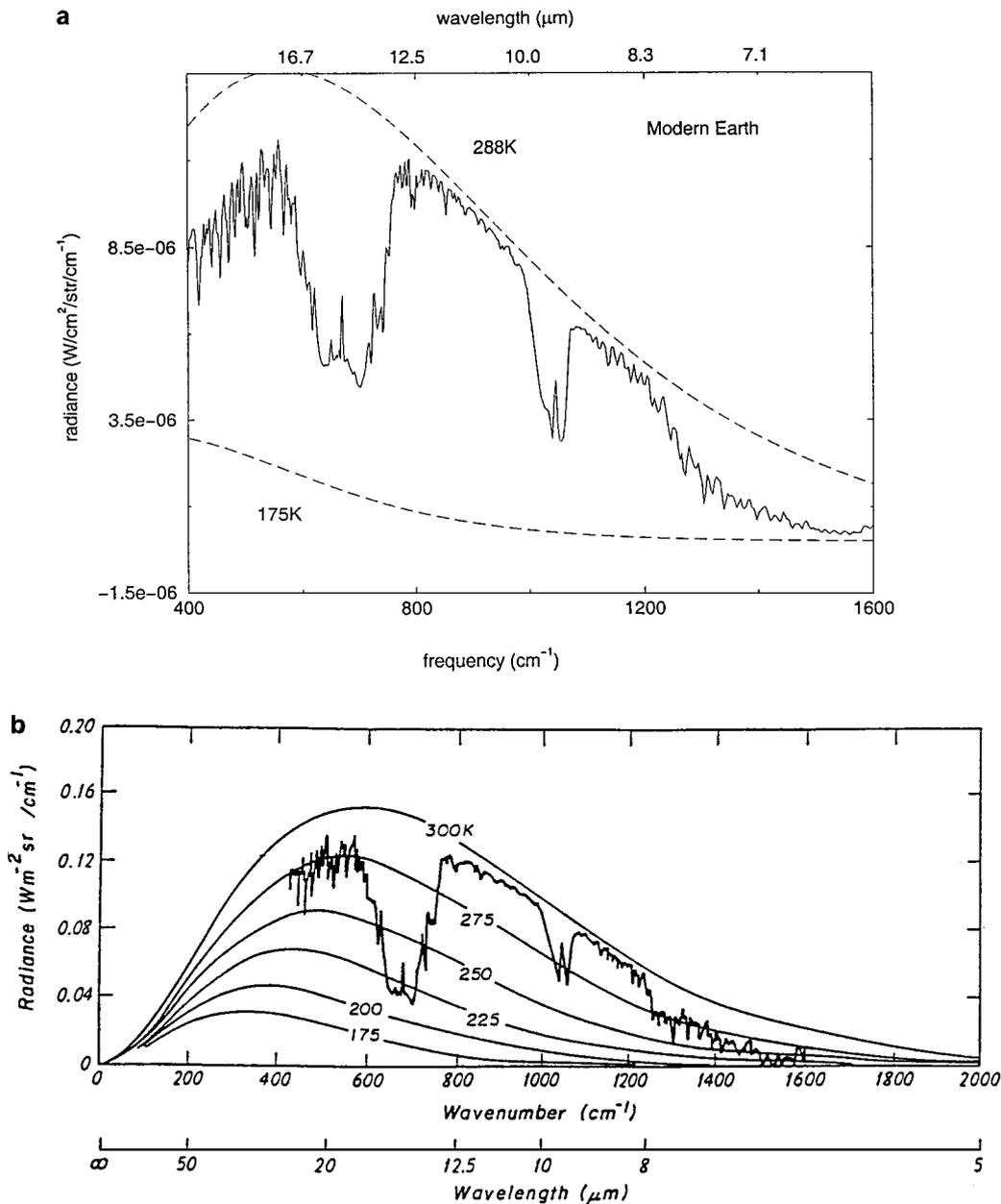
FIG. 1. (a) A synthetic spectrum of the modern Earth atmosphere, as generated by LBLRTM. The assumed surface temperature (T_s) is 288 K. (b) The actual spectrum of Earth's atmosphere as measured by a scanning interferometer aboard the *Nimbus 7* satellite during a pass over the North African desert ($T_s = 296$ K) (Liou 1992). From "Radiation and cloud processes in the atmosphere: theory, observation, and modeling" by Kuo-Nan Liou. © 1992 by Oxford University Press, Inc. Used by permission.

of TPF has yet to be determined, it is planned that $\lambda/\Delta\lambda$ will be somewhere between 3 and 300. The high-resolution spectra that we obtained from LBLRTM were therefore degraded to similar resolution (~200 in the middle of the range) to approximate the spectra we might expect to obtain from TPF. We modeled five different profiles: A modern Earth profile based on the U.S. standard atmosphere (NOAA-S/T76-1562), and four profiles where we set the oxygen content at 10^{-1}, 10^{-2}, 10^{-3}, and 10^{-4} times present atmospheric level (PAL). The pressure and temperature profiles for the latter four followed that of the U.S. standard atmosphere up to the tropopause (10 km). Above that

height, the temperature was assumed to decline adiabatically to 175 K and to remain constant above that. This change was made to compensate for the lack of warming from UV absorption by ozone. Eventually, this calculation should be done with a coupled photochemical/radiative–convective climate model that calculates the stratospheric temperature self-consistently, but for now we have simply assumed that the stratospheric temperature bulge disappears at O_2 levels below 1 PAL.

Under these assumptions, the equivalent width of the 9.6-μm ozone band (and the 15-μm CO_2 band) increases with respect to the modern atmosphere when the O_2 abundance is reduced to
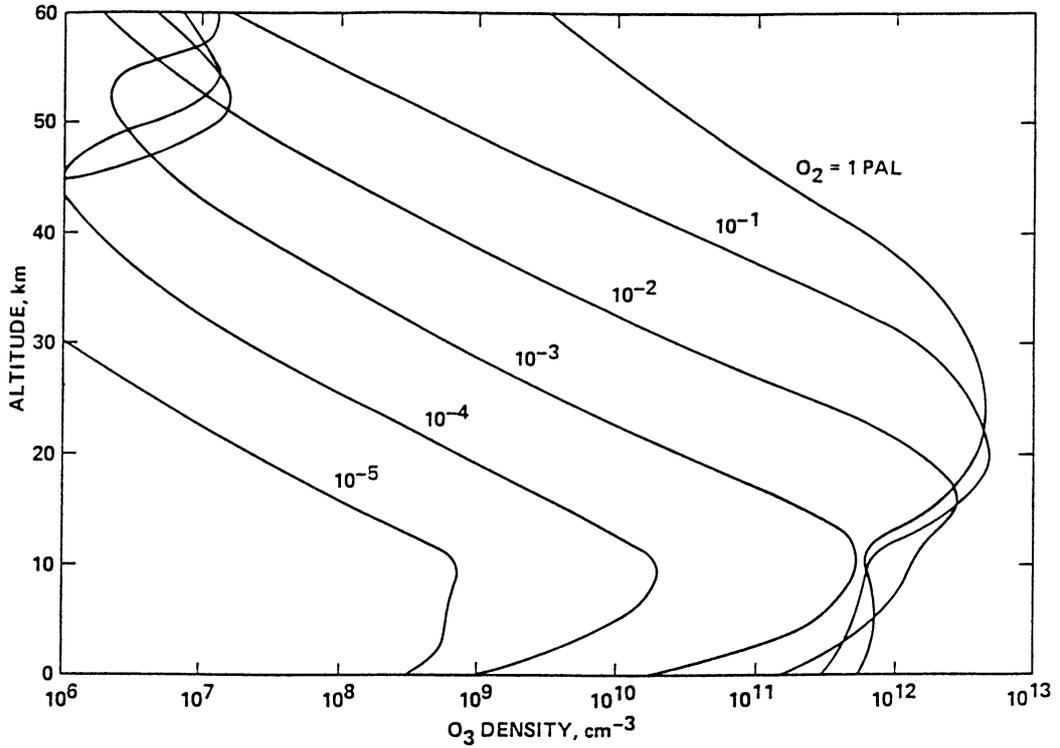
FIG. 2. Ozone profiles for different atmospheric O_2 concentrations, generated from the model of Kasting *et al.* (1985), but previously unpublished.
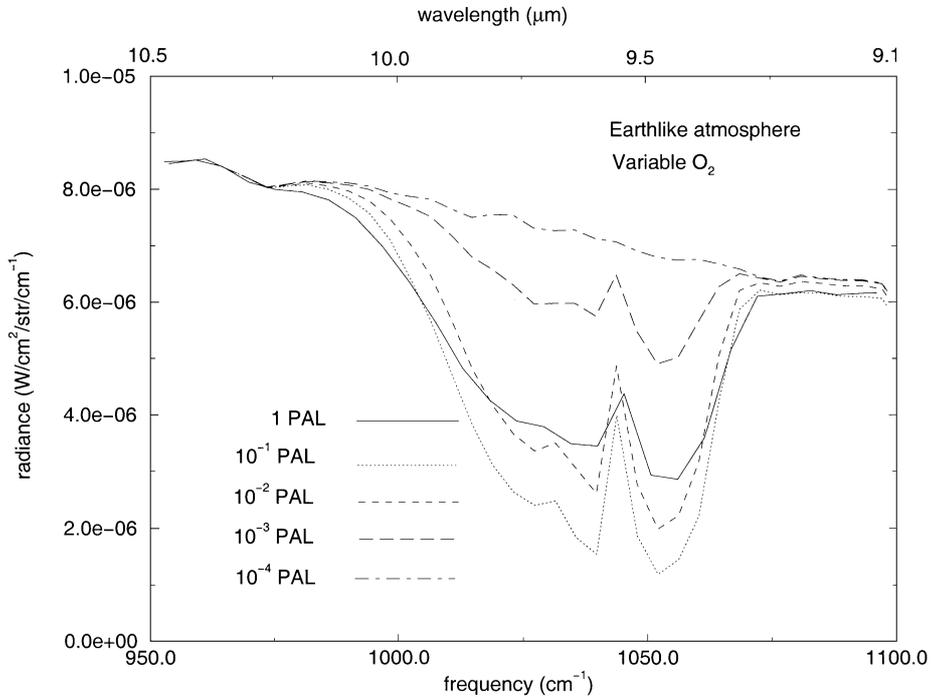
FIG. 3. The modeled 9.6-mm ozone band for an Earth-like atmosphere containing variable amounts of O_2. A cold, isothermal stratosphere (175 K) was assumed for all but the 1 PAL case.

10^{-1} PAL (Fig. 3). This is partly the effect of assuming a low-temperature stratosphere; a coupled photochemical/temperature calculation might not produce the same result. However, Fig. 3 suggests that ozone should be observable down to concentrations of at least 10^{-2} PAL of O_2, so it is indeed a sensitive indicator of the presence of O_2.

SYNTHETIC SPECTRA OF POSSIBLE "FALSE POSITIVE" TERRESTRIAL PLANETS

A critical question for TPF is whether it is possible to get a false positive result, that is, to see O_3 (and, by implication, O_2) on an uninhabited planet. Kasting (1997) has identified two cases where this might happen. The first is a "Venus-like" planet that loses water rapidly as a consequence of a runaway greenhouse, or some variant thereof . After the hydrogen has escaped over a period of a few tens or hundreds of millions of years, O_2 could conceivably build up to concentrations of tens or hundreds of bars before it eventually reacts with the planet's surface. The second false positive case is a "Mars-like" planet that is too small to generate sustained volcanism and too cold to have liquid water at its surface. Under such circumstances, O_2 produced from H_2O photodissociation followed by hydrogen escape could accumulate to appreciable levels in the atmosphere because the available O_2 sinks would be small. O_2 formed from the photolysis products of CO_2 (Nair *et al.* 1994) would accumulate as well. We note that Mars' atmosphere contains 0.1% O_2 by volume and might contain even more if it were slightly larger and, hence, did not lose oxygen to space by nonthermal processes (McElroy 1972).

Hopefully, future interpretations of TPF data will be able to identify such planets from their positions with respect to their parent star's habitable zone. (The Venus-like planet is, by definition, outside the inner edge, and the Mars-like planet is outside the outer edge.) But the actual boundaries of the habitable zone, which have been estimated using one-dimensional climate models (Kasting *et al.* 1993a), may in reality be difficult to pin down because of the highly uncertain climatic effects of clouds (see, e.g., Forget and Pierrehumbert 1997). In order to investigate how these planets might appear to TPF, we have computed synthetic spectra for planets that are representative of these two cases.

For our Venus-like planet, we assumed a "moist greenhouse" scenario (Kasting 1988). We further assumed that the atmosphere of early Venus had an initial mixture of gases similar to that postulated for the early Earth, and that it initially had liquid water on its surface. The surface temperature would have been roughly 353–373 K before the escape of the planet's H_2O inventory. An atmosphere with this surface temperature would have remained saturated with water vapor up to very high altitudes. The stratosphere would be wet in such a scenario, allowing rapid photodissociation of H_2O followed by hydrogen escape to space. Eventually, this process depleted Venus of water, preventing the loss of CO_2 by silicate weathering and leading to the current thick, hot atmosphere.

We assumed a 1-bar mixture of CO_2 and N_2 at the surface, in the proportion of 1 : 4 (the same as the early-Earth case described in the next section). We set the surface temperature equal to 373 K and added H_2O with a vapor pressure of 1 bar, as would be expected if the planet had an ocean. The total surface pressure was therefore 2 bars. We calculated a moist-adiabatic temperature and pressure profile (Fig. 4) based on equations from Kasting (1988, Appendix A) and used this to compute the results shown in Fig. 5. The atmosphere was modeled to a height of 120 km in this case to ensure accuracy in the presence of large amounts of stratospheric H_2O. The only easily identifiable features in the spectrum are the 15-μm CO_2 band and water vapor bands longward of 12 μm and shortward of 7.5 μm. Because of its high H_2O content, the atmosphere is quite opaque in the region of the spectrum we are modeling; the lower blackbody curve indicates the temperature at the top of our model atmosphere (120 km), while the upper curve is the temperature at an altitude of 46 km.

While we would expect much O_2 to be generated during the H-escape phase of the early venusian atmosphere, the production of ozone from this O_2 would most likely be suppressed by the presence of abundant odd hydrogen species generated by the photolysis of H_2O. Only after the atmosphere of Venus had lost all of its water would we expect ozone abundance to rise to appreciable levels. Thus, criteria for evaluating the likelihood of the existence of life on a planet bearing such an atmosphere become apparent: if we see ozone, but no water, we may tentatively conclude that the planet has experienced the same fate that seems to have befallen Venus, and that its O_2 and O_3 are entirely abiotic in origin.

For the Mars-like planet we assumed a temperature profile similar to that of modern Mars, with a surface temperature of 215 K, decreasing adiabatically to an isothermal stratospheric temperature of 180 K. The atmospheric composition was a Mars-like mixture of gases (95% CO_2, 3% N_2, 0.1% O_2, and 0.08% CO). We assumed a 1-bar surface pressure, which of course is much higher than the present martian surface pressure (6 mbar), but which might be appropriate for an Earth-sized planet situated just outside the habitable zone around its parent star. As Fig. 6 illustrates, the spectrum is dominated by CO_2 features: the 15-μm band, two "hot" bands at 9.4 and 10.4 μm (corresponding to transitions between the v_3 and v_1 vibrational modes), and two bands at 7.9 and 7.3 μm, representing the v_1 fundamental bands of the isotope $^{12}C^{16}O^{18}O$ (Rothman *et al.* 1992). These are observed here, but not in our early-Earth-type model atmosphere (next section), because of the much lower amount of H_2O in this very cold atmosphere. The lack of a strong H_2O rotation band longward of 12 μm and the absence of the H_2O vibrational bands shortward of 7.5 μm should make this type of planet easy to identify.

METHANE AS A POSSIBLE INDICATOR OF LIFE

While ozone would be an effective indicator of photosynthetic life, the absence of an ozone signal does not necessarily imply

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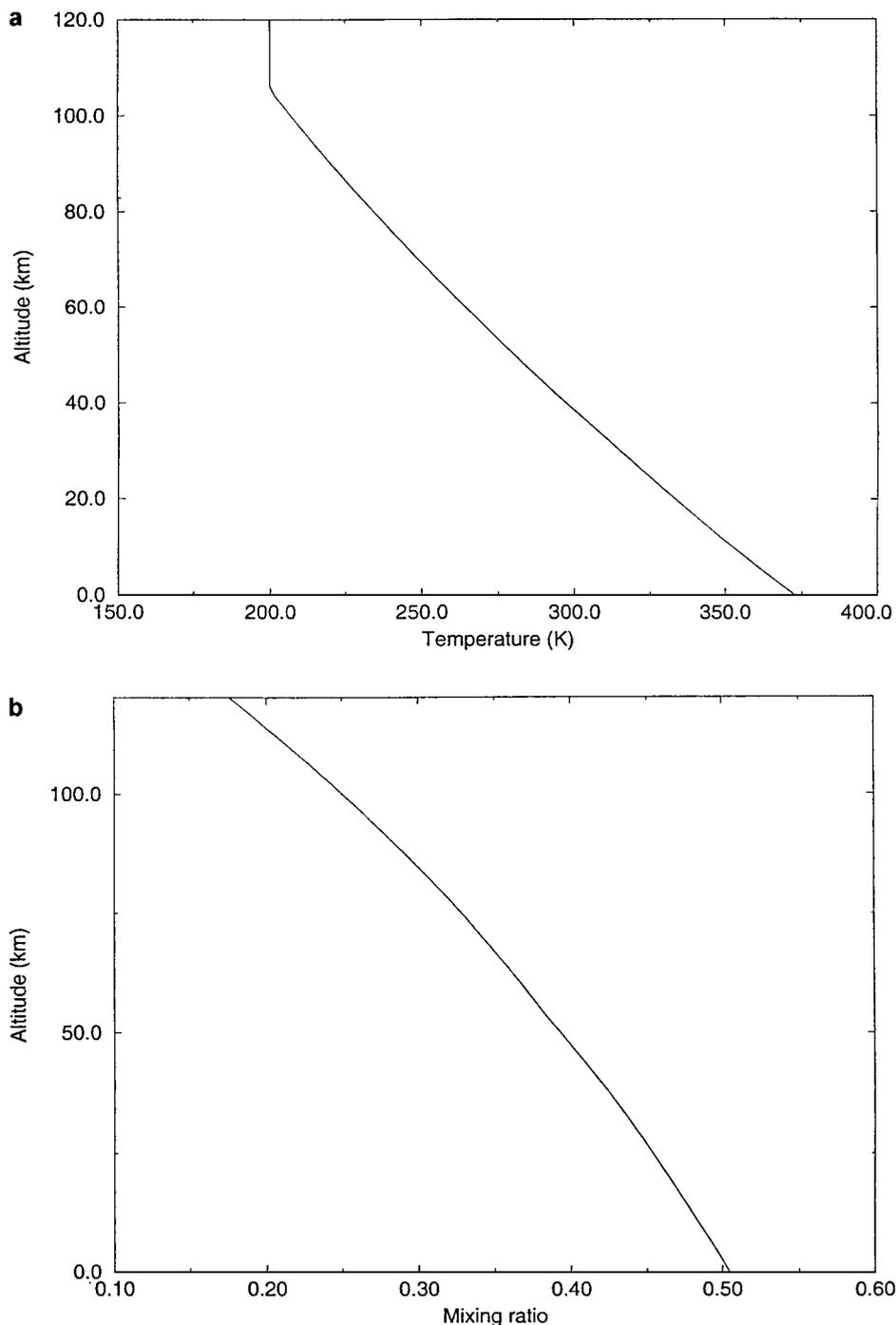
FIG. 4.   (a) Temperature and (b) mixing ratio profiles used for the early Venus case.

that life is not present. For example, free O_2 has probably been present in appreciable amounts in the Earth's atmosphere for only the past 2 billion years (Cloud 1972, Walker *et al.* 1983, Holland 1994) (see Ohmoto 1996, for a dissenting opinion); yet the oldest signs of life go back as far as 3.9 billion years (Mojzsis *et al.* 1996). Photosynthetic life may well have been present at this very early time, but if so, the O_2 produced was immediately consumed by reaction with reduced volcanic gases.

Early organisms may also have utilized non-O_2-producing metabolic processes, such as anoxygenic photosynthesis and methanogenesis (Walker 1977). The latter process is particularly interesting from a life detection standpoint because it produces CH_4. CH_4 has a small abiotic source from volcanic outgassing at the midocean ridges today (Welhan 1988, Kasting and Brown 1998), but its primary sources are biological (Watson *et al.* 1990). In today's atmosphere, methane would be extremely
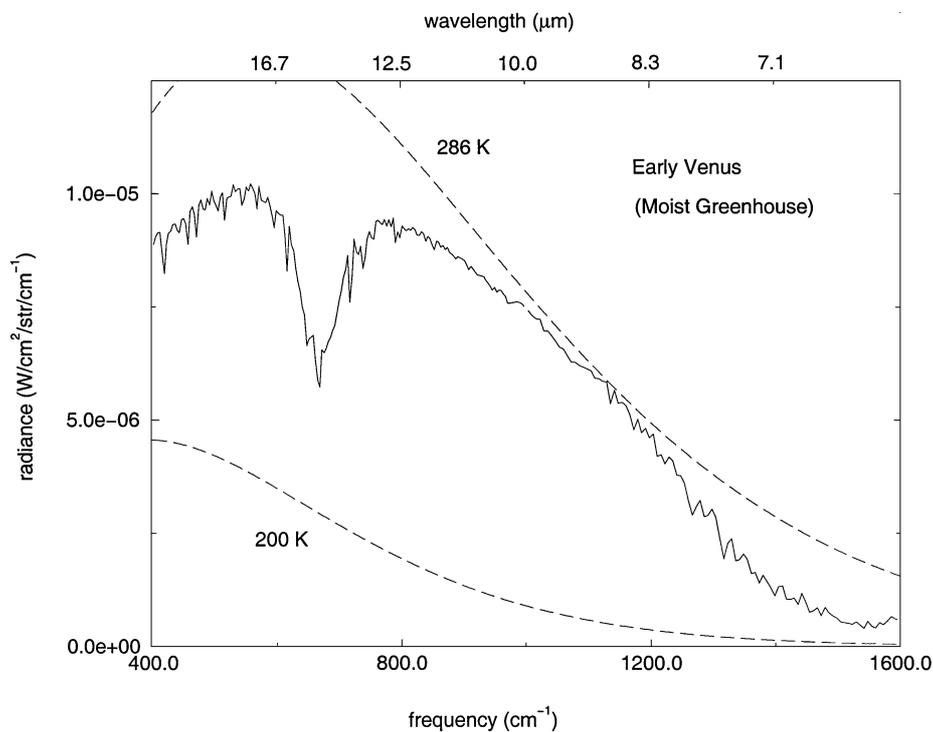
FIG. 5. Synthetic spectra of an "Early Venus-like" planet with a moist greenhouse atmosphere. The 286-K level occurs at approximately 46 km altitude.
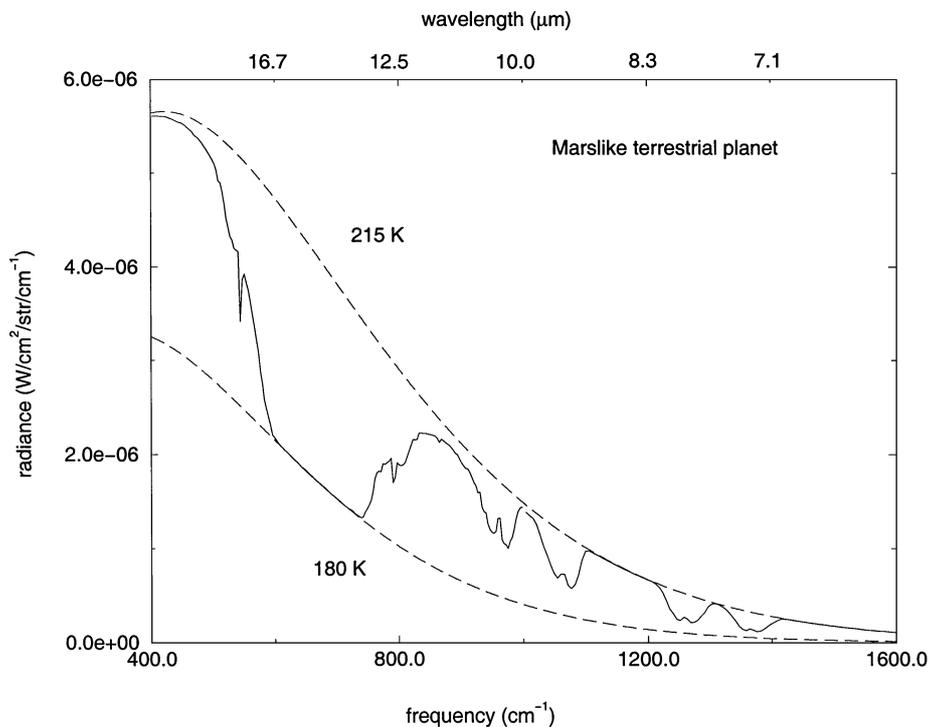
FIG. 6. Synthetic spectra of the atmosphere of a "Mars-like" terrestrial planet. The surface pressure is 1 bar, the surface temperature is 215 K, and the stratospheric temperature is 180 K.

difficult to detect with an instrument like TPF, as it is mostly confined to the troposphere and is present in such small amounts ($\sim$1.7 ppm). Before the rise of O_2, however, methanogenic life may have generated a methane-rich atmosphere which TPF could have detected. We now demonstrate that observation of methane in the atmosphere of extrasolar planets is feasible, and we speculate about what such an observation might tell us about the presence of life on a planet's surface.

SYNTHETIC SPECTRA OF EARTH-LIKE CH₄-RICH ATMOSPHERES

The first step in demonstrating the usefulness of methane as a biomarker is to show that it is detectable by a low-resolution spectrometer such as TPF. To do this, we applied the LBLRTM code to model atmospheres consisting of 0.78-bar N_2 and 0.20-bar CO_2 at the surface. This is a typical (though by no means unique) composition suggested for the early atmosphere of Earth (Walker 1977). A modern water vapor profile was assumed, with a mixing ratio of 1.2% at the surface falling off with a scale height of 2 km. The temperature and pressure profiles were the same as those for the low-O_2, Earth-like cases. Spectra were computed for methane mixing ratios of 0, 1, 100, and 10^4 ppm, and are illustrated in Fig. 7. Once again, these spectra should be considered as "preliminary." In reality, absorption of visible and near-IR radiation by CH_4 would raise the temperature of the stratosphere at high CH_4 concentrations, so the depth of the absorption bands might be less than we have calculated.

For the low-CH_4 atmospheres the spectra are dominated by the strong CO_2 band at 15 μm, the two hot CO_2 bands at 9.4 and 10.4 μm, the pure rotation band of H_2O longward of approximately 12 μm, and the vibration–rotation bands of H_2O shortward of approximately 8 μm. The difference between the 1 ppm methane case and that containing no methane is small; it is unlikely that these two cases would be distinguishable based on TPF observations. However, the 100-ppm methane case shows significant absorption from the strong 7.6-μm band of CH_4. In the 10^4 ppm, or 1%, methane case this band is completely opaque (so the brightness temperature in this spectral region is equal to our assumed stratospheric temperature of 175 K). The 7.6-μm band of CH_4 is clearly separated from the main CO_2 and H_2O bands and should be observable by TPF for planetary atmospheres in which the CH_4 mixing ratio exceeds 100 ppm.

DISCUSSION

In order to decide whether methane might be used as a biomarker, we need to estimate the possible source terms for methane on an abiotic, Earth-like planet. There are at least three known mechanisms for the abiotic production of methane. The first is the reduction of CO_2 during the low-temperature serpentization of olivine (Berndt *et al.* 1996). Although this mechanism may be widespread, long residence times of CO_2 in ultramafic rock appear to be needed to produce significant amounts
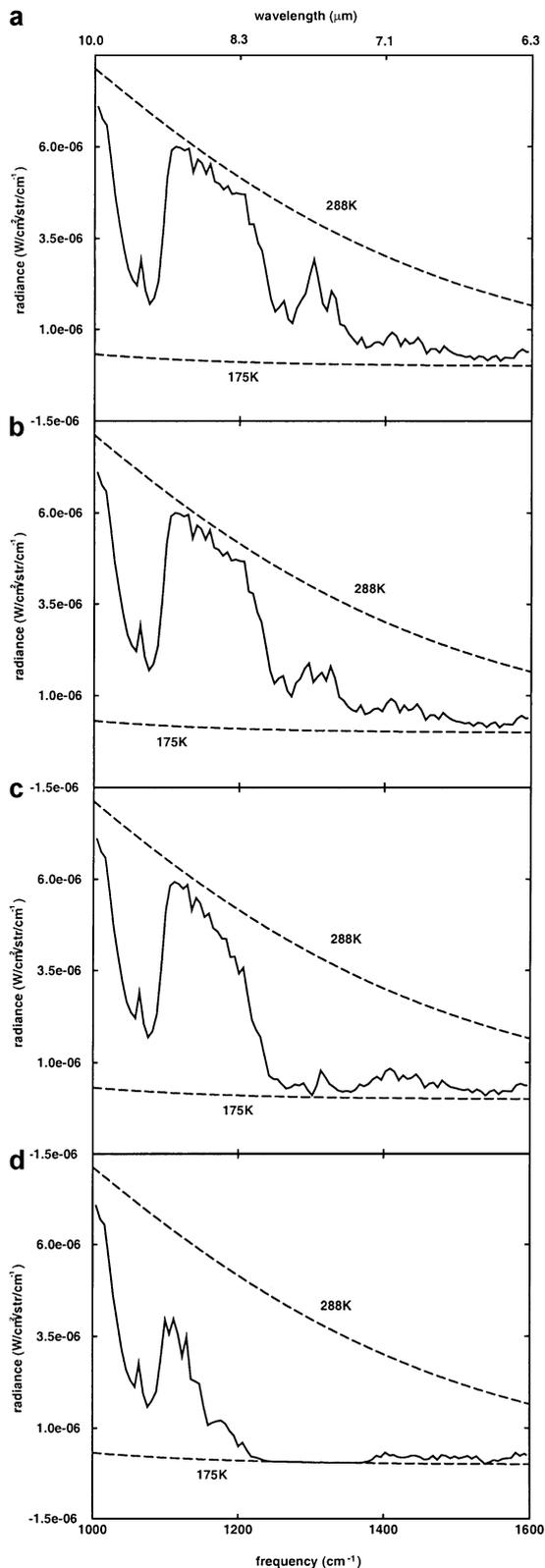
FIG. 7. Synthetic spectra of a primitive Earth-like atmosphere containing 0.8 bar N_2 and 0.2 bar CO_2, along with: (a) no CH_4, (b) 1 ppm CH_4, (c) 100 ppm CH_4, and (d) 10^4 ppm (1%) CH_4. The signature of methane is easily observable for CH_4 concentrations down to 100 ppm.

of methane. Thus, this process is probably less important than other abiotic sources of methane.

A second mechanism for abiotic methane generation is the photolysis of H_2O in the presence of CO (Wen *et al.* 1989), which also generates a number of other reduced carbon compounds such as aldehydes, alchohols, alkanes, and alkenes. For methane production, the net reaction is

$$2H_2O + 4CO \rightarrow CH_4 + 3CO_2.$$
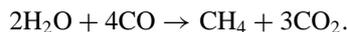
This mechanism, however, appears to be very inefficient. In the model of Wen *et al.* (1989), the resultant methane mixing ratio was approximately 4×10^{-8}. This is about 40 times less than the average methane mixing ratio of 1.7×10^{-6} on present-day Earth, which is mostly biogenic. Experiments with our own photochemical model (Brown 1999) at different atmospheric CO_2 and CO mixing ratios indicate that this mechanism never produces significant quantities of methane. This mechanism can therefore be safely ignored for our purposes.

The third source of abiotic methane is volcanism. While little or no methane is generated from modern surface volcanism (Holland 1984), conditions at the midocean ridges of present-day Earth are more favorable for its production. Indeed, the observed ratio of CH_4/CO_2 in unsedimented midocean ridge hydrothermal vent fluids is on the order of 1–2% (Welhan 1988). The total outgassed carbon flux at the midocean ridges is approximately 1.4×10^{12} mol/yr, or 5×10^9 molecules cm^{-2} s^{-1} (DesMarais and Moore 1984, Marty and Jambon 1987, Kasting and Brown 1998). Hence, the current flux of CH_4 from submarine volcanism is approximately 5×10^7 molecules cm^{-2} s^{-1}. A photochemical model of a weakly reducing atmosphere which includes such a CH_4 flux indicates that the corresponding CH_4 mixing ratio would be ~0.5 ppm (Fig. 8) (Kasting and Brown 1998, Brown 1999). This model is similar to those described by Kasting *et al.* (1983) and Zahnle (1986), except that it also includes sulfur and ammonia photochemistry.

It is possible, even probable, that the abiotic production of methane from submarine vents was once much higher than it is today. If the mantle was once highly reduced, as suggested by Kasting *et al.* (1993b) (see also Kadik 1997, and Righter and Drake 1997), then the CH_4/CO_2 ratio could have been much higher. If most of the carbon outgassed from the midocean ridges was emitted as CH_4, the atmospheric CH_4 mixing ratio could have been 50 ppm or more, depending on the overall release rate of carbon compared to that of today (Fig. 8).
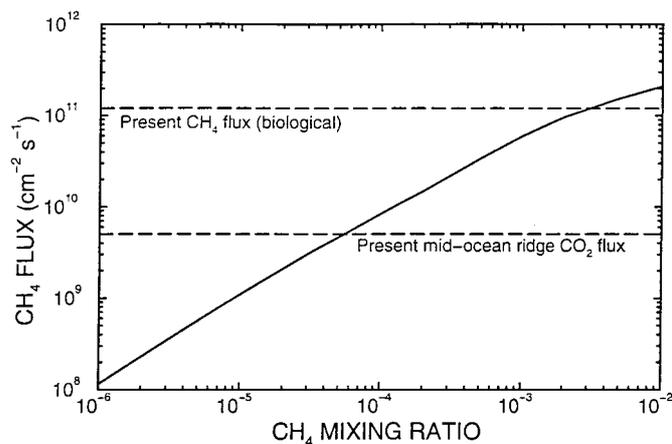
Even with a highly reduced mantle, however, the abiotic CH_4 flux from Earth is still much lower than the present biological CH_4 flux. The present biological CH_4 flux is on the order of 2.8×10^{13} mol/yr, or approximately 1×10^{11} CH_4 molecules cm^{-2} s^{-1} (Watson *et al.* 1990, Kasting and Brown 1998). This is about 20 times higher than the total carbon flux at the midocean ridges. It is difficult to estimate the biological CH_4 flux on the early Earth, but if it was similar to today, then the atmospheric CH_4 mixing ratio could have been on the order of 3×10^{-3} (Fig. 8). Whether this is high enough to distinguish it from abiotically produced CH_4 is unclear. Consequently, observed atmospheric CH_4 levels near or exceeding 3×10^{-3} would be suggestive of biological activity, but it would be difficult to prove that they required biological activity. A young, volcanically active planet with a highly reduced mantle might produce a comparably high level of atmospheric CH_4 and a similar spectral signature.

An additional caveat that should be added to this analysis is that the high atmospheric CH_4 levels predicted by Fig. 8 for a biologically active planet may only be possible if the escape rate of hydrogen is less than the diffusion-limited rate. At the diffusion limit (Hunten 1973, Walker 1977), a CH_4 mixing ratio of 3×10^{-3} would imply an H escape rate of approximately $(2.5 \times 10^{13})(4)(3 \times 10^{-3})$, or 3×10^{11} H atoms cm^{-2} s^{-1}. By comparison, the total outgassing rate of reduced gases today is only enough to supply an escape flux of approximately 1×10^{10} H atoms cm^{-2} s^{-1} (Holland 1978, pp. 291–292; Kasting and Brown 1998). Thus, a CH_4 mixing ratio of 3×10^{-3} or more requires reduced volcanic gas fluxes at least 30 times higher than today. Alternatively, this mixing ratio could be supported if hydrogen escapes at less than the diffusion-limited rate. This latter possibility is not at all physically implausible. An anoxic, CO_2-dominated primitive terrestrial atmosphere should have a cold (~400 K) exosphere, just as Mars and Venus do today. Therefore, it may be energetically difficult for hydrogen to escape at rates exceeding 10^{10} H atoms cm^{-2} s^{-1}. (The present H escape rate for Earth is only about 3×10^8 H atoms cm^{-2} s^{-1}.) More work needs to be done to evaluate hydrogen escape mechanisms for H_2- or CH_4-rich atmospheres so that we can better estimate what atmospheric CH_4 levels might have been on the primitive Earth, and what might be expected on similar types of planets orbiting other stars.

CONCLUSIONS

Ozone, with its very strong 9.6-μm band, appears to be a robust indicator of the existence of O_2 in the atmosphere of a planet. An instrument with the resolving power of TPF should be able to discern this feature for amounts of O_2 greater than

FIG. 8. The surface CH_4 flux required to support various atmospheric CH_4 mixing ratios in a weakly reducing primitive atmosphere (from Kasting and Brown 1998). Reprinted with the permission of Cambridge University Press.

1×10^{-2} PAL. O_2 and O_3 may accumulate abiotically on certain Venus- and Mars-like planets, but such planets should be distinguishable from inhabited planets by their spectra and by their position outside of the boundaries of the liquid water habitable zone.

The strong 7.6-μm band of methane provides a spectral signal that should be observable by an instrument like TPF for atmospheric CH_4 concentrations exceeding $\sim$100 ppm. CH_4 concentrations of this magnitude could be produced by either biotic or abiotic sources if the planet in question had an anoxic CO_2–N_2 atmosphere similar to that expected for early Earth. CH_4 concentrations of 3000 ppm (3×10^{-3} mixing ratio) or higher would require a CH_4 source comparable to the present biological CH_4 flux on Earth and may therefore be a useful, though not definitive, indicator of extraterrestrial life. While the use of methane as a biomarker gas lacks the certainty the detection of ozone would provide, it has the advantage of allowing us to extend our search for extrasolar life to a wider variety of planets.

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