The Early Faint Sun Paradox: Organic Shielding of Ultraviolet-Labile Greenhouse Gases

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Atmospheric mixing ratios of $\sim 10^{-5 \pm 1}$ for ammonia on the early Earth would have been sufficient, through the resulting greenhouse warming, to counteract the temperature effects of the faint early sun. One argument against such model atmospheres has been the short time scale for ammonia photodissociation by solar ultraviolet light. Here it is shown that ultraviolet absorption by steady-state amounts of high-altitude organic solids produced from methane photolysis may have shielded ammonia sufficiently that ammonia resupply rates were able to maintain surface temperatures above freezing.

The compositions and surface pressures of the early atmospheres of Earth and Mars after the end of the heavy bombardment are unknown. Models for Earth range from reducing atmospheres with surface pressures $p_s \sim 1$ bar (*1*) to $p_s \sim 10$ bar of CO_2 (*2*). Atmospheres near a neutral oxidation state are currently favored for two reasons. First, a vast reservoir of CO_2 is present in Earth's sediments in the form of carbonates ($p_s \simeq 60$ bar) and in the atmosphere of Venus ($p_s \simeq 90$ bar). This carbon reservoir could have been in the early atmosphere partly as CO or CH_4 if some abundant reducing agent were present. However, metallic iron, one possible agent, is thought to have been segregated from the surface early and quickly during core formation (*3*), suggesting that carbon was present in the atmosphere primarily as CO_2. The presence of other reduced gases such as NH_3 also depends on the oxidation state of the upper mantle. If early continents were largely absent, the resulting inhibition of carbonate sedimentation may have led to dense CO_2 atmospheres; Kasting (*4*) estimates that $p_s(CO_2)$ was 0.1 to 10 bar 4 billion years ago (Ga). However, it is possible that the mantle may be more reducing than once thought (*5*), and geochemical arguments for early atmospheric composition are not yet conclusive. A second argument for an early atmosphere that was in a neutral oxidation state comes from photochemical kinetics, which suggests that atmospheric NH_3 and CH_4 would be photodissociated by solar ultraviolet (UV) radiation on short time scales (*6–9*). Here we argue instead that photodissociation of CH_4 may have led to the production of a high-altitude organic aerosol that absorbed UV rays and allowed reducing gases to exist for much longer times. If this is correct, the second of the two arguments against reducing gases in the early atmosphere is no longer compelling, with implications for the origin of life and the resolution of the early faint sun paradox.

The origin of life requires sources of preexisting organic molecules, which are much more readily generated in reducing rather than in neutral oxidation-state atmospheres (*10*). With allowance for exogenous sources, reducing atmospheres give organic mixing ratios in the early oceans some three orders of magnitude higher than those for neutral atmospheres (*11*). Thus, models for Earth's primitive atmosphere that postulate no significant abundance of reduced gases suffer the drawback that the origin of life is more difficult to understand.

The Early Faint Sun Dilemma

The equilibrium temperature of an airless, rapidly rotating planet is $T_e \equiv [SR^2(1 - A)/4a^2\varepsilon\sigma]^{1/4}$, where σ is the Stefan-Boltzmann constant, ε the effective surface emissivity, A the wavelength-integrated Bond albedo, R the planet's radius, a the planet's distance from the sun, and S the solar constant at a. For Earth today, $T_e \simeq 255$ K, and the difference $\Delta T \simeq 33$ K between T_e and the observed mean surface temperature T_s is due to the mainly H_2O-CO_2 atmospheric greenhouse effect. Stars like the sun increase their luminosity through time as the hydrogen in the star's core is converted to helium. Estimates of the change in S between 4 Ga and today are $\simeq 0.25S_0$ (*12*), with an error of about $\pm 0.1S_0$, where S_0 is the present-day value. Holding A, ε, a, and the CO_2 mixing ratio constant at their current values for Earth, and letting the H_2O abundance be determined by its equilibrium vapor pressure, Earth's $T_s < 0$°C about 2 Ga (*13–15*). Allowance for an ice-albedo feedback implies a fully glaciated planet as recently as 1 Ga (*16*). These results contradict geological evidence for abundant, globally distributed liquid H_2O before 3 Ga (*13, 14, 17, 18*). The discrepancy is enhanced by evidence that before 2.5 Ga, Earth may have been considerably warmer than it is today (*19*). The implications are even more severe for Mars; yet there is strong evidence for liquid water on Mars 3.5 to 4.0 Ga (*20*).

This early faint sun paradox is only a paradox if we insist on holding A, a, ε, and greenhouse warming constant over time. Were $A = 0.3$ at 4 Ga, as it is today, T_e would have been 237 K (*21*); even if A had been 0 at 4 Ga, T_e would still have been only 259 K. In models of an all-ocean early Earth with a 14-hour day, simulated temperatures rise only an additional 5.5 K (*22*). Likewise, at most a few degrees can be pried out of plausible long-term variations in infrared emissivity. Although some low-mass planets can chaotically migrate in heliocentric distance a over 4 billion years (*23*), there is no evidence for the steady increases in a for Earth by the ~10% necessary to have compensated for the increase in S over its history. Another suggestion proposes that the early sun lost ~10% of its mass, producing a solar flux at Earth before ~4 Ga greater than its current value (*24*); however, there is as yet no clear evidence for such mass loss (*25*). Convolving the rapid rotation of Earth, an all-ocean planet, extremely low albedo, and a small solar mass loss, it is possible that early Earth reached 0°C but not much warmer temperatures. Such a conglomerate explanation seems strained. We therefore reconsider changes in greenhouse warming.

The Wien peak of Earth's blackbody emission 4 Ga, as today, laid at 8 to 14 μm, a window in the combined absorption spectra of H_2O and CO_2 at pressures below a few bars and temperatures < 300 K. Because small quantities of NH_3 provide considerable opacity around 10 μm, Sagan and Mullen (*13, 14*) proposed a volume mixing ratio for NH_3 ($[NH_3]$) of $\sim 10^{-5}$, pressure-broadened in an ~1-bar atmosphere, as the solution to the early faint sun dilemma for Earth and Mars. Subsequent calculations (*6, 15*) confirm that $[NH_3] \sim 10^{-5 \pm 1}$ would suffice. In comparison, background abundances in Earth's current O_2 atmosphere are $[NH_3] \sim 10^{-8}$ (*26*). These NH_3 abundances represent a steady state after

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loss processes, including oxidation, rainout, high-altitude photolysis, and reaction with CO_2. Globally averaged, $[NH_3] \sim 10^{-2}$ $[CH_4]$ today.

Although NH_3 is soluble in water and subject to rapid rainout (*27*), there is, in the absence of photolysis, an equilibrium atmospheric abundance determined by oceanic mineral equilibria. Independently, a lower limit can be derived from the requirement that the deamination of aspartic acid, a key amino acid for the origin of life, be reversed. Bada and Miller (*28*) thereby found $[NH_3]$ for early Earth to be 10^{-7} at 0°C, 3×10^{-5} at 25°C, and 3×10^{-4} at 50°C, consistent with the $10^{-5 \pm 1}$ derived from the greenhouse requirement. Other estimates lie in a similar range (*29*).

All organisms on Earth are able to metabolize NH_4^+ (*30*). Few organisms can process N_2 directly, and ubiquitous metabolic facility with NH_4^+ may be a remnant from earlier times when atmospheric NH_3 was readily available (*31*). These chemical and biological arguments independently point to NH_3 as a minor constituent of the primitive atmosphere.

NH_3 Photolysis and CO_2 Greenhouses

Photochemical kinetics demonstrates that $[NH_3] \sim 10^{-5}$ would be photodissociated by the solar UV continuum at wavelengths $\lambda < 2300$ Å and irreversibly converted into N_2 within decades (*6, 8, 9*). Likewise, $[CH_4] \sim 10^{-5}$ would be photolyzed within centuries. These time scales are so short that hypotheses about resupply (*13, 14*) seem wholly without merit; an NH_3 outgassing rate $\sim 5 \times 10^{15}$ g year^{-1} would be required to keep pace with photolysis, which implies $\sim 10^3$ bar of N_2 built up over ~1 billion years, contradicting current atmospheric and sedimentary rock inventories.

Owen *et al.* (*8*) proposed that massive amounts of CO_2 might close the 8- to 14-μm window and provide the missing greenhouse effect. Numerous calculations have since shown that a few bars or less of CO_2 might suffice to raise the surface temperature of Earth 4 Ga to several tens of degrees Celsius (*15, 32*). But Rye *et al.* (*33*) argue from the absence of siderite in paleosols that $[CO_2]$ between 2.75 and 2.2 Ga was $\leq 10^{-1.4}$ bar, implying that greenhouse gases other than CO_2 contributed to greenhouse warming in the late Archean and early Proterozoic eons. For Mars, there is extensive evidence for ancient outflow channels and valley networks (*20*), some evidence for lakes (*34*), and even an argument for oceans (*35*) 3 to 4 Ga. The general opinion has been that this evidence requires a massive early greenhouse effect on Mars (*14, 15, 36*), but the higher early subsurface thermal gradient eases the greenhouse demands (*37*). Massive CO_2 greenhouse models face challenges from CO_2 condensation (*38*) and the difficulty in finding sufficient corresponding martian carbonate sediments (*39*).

Ultraviolet Shielding

Given doubts about massive CO_2 atmospheres for Earth and Mars, we reexamine models of comparatively thin atmospheres in which minor constituents provide the needed infrared opacity. We ask whether, with no ad hoc assumptions, there is a way to shield NH_3 and other UV-labile gases so that demands on the resupply rate are reasonable. Methane can be dissociated only by UV photons of $\lambda < 1450$ Å (the dissociation is therefore entirely dominated by solar Lyman α radiation), whereas NH_3 photolysis is driven by UV at wavelengths as long as 2300 Å. This longer wavelength UV, which in total energy flux exceeds that of $\lambda < 1450$ Å UV by more than two orders of magnitude, penetrates deeper into the atmosphere. The result is that whereas CH_4 photolysis is expected to occur high in the atmosphere (*40, 41*), photolysis of NH_3 should occur at a lower altitude, with NH_3 photolysis products spatially separated from those of CH_4 (*6*).

Photochemical modeling indicates that NH_3 photolysis, for $[NH_3] \sim 10^{-5 \pm 1}$, peaks at altitudes of 25 to 35 km, depending on $[NH_3]$ and the assumed eddy diffusion coefficient (*6*). Zahnle (*42*) has modeled the altitude at which $[CH_4]$ photolysis and polymerization should occur as a function of $[CH_4]$, $[CO_2]$, UV flux, and eddy diffusion profile. For contemporary values of the eddy diffusion profile and $[CO_2]$, he finds the altitude of CH_4 polymerization ranging from 40 to 75 km (*43*) as $[CH_4]$ varies from 10^{-5} to 6×10^{-4} (corresponding to CH_4 fluxes into the atmosphere ranging from 5×10^{10} to $\sim 4 \times 10^{11}$ cm^{-2} s^{-1}). In all cases, he takes $[H_2O]$ at the base of the stratosphere to be 4×10^{-6}; that is, CH_4 polymerization is not prevented by OH generated from UV dissociation of H_2O (*44*). However, a transition from oxidation of CH_4 to polymerization occurs when the local C/O ratio passes through unity, at which point large percentages of CH_4 are polymerized. The CH_4/CO_2 ratio is therefore important.

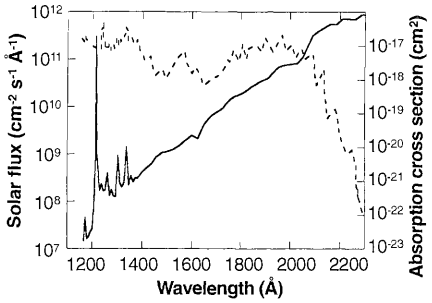

Fig. 1. Solar UV flux at Earth (solid line) and the absorption cross section of NH_3 (dashed line) as a function of wavelength. With the exception of the Lyman α spike at 1216 Å, solar UV flux drops quickly shortward of 2000 Å, whereas NH_3 absorption falls rapidly longward of 2000 Å.

Organic solids from atmospheric shocks (as well as interplanetary dust particles) contribute to a high-altitude layer of organic aerosols, depending on atmospheric composition (*11*). If CH_4 photolysis and other processes produce an organic haze, which in turn provides UV shielding to greater depths (the C_2 hydrocarbons absorb at considerably longer wavelengths than CH_4), NH_3 will lie below this screen and be substantially shielded from photolysis. Experimentally, N_2-CH_4 gas mixtures with $[CH_4] \sim 10^{-3}$ generate upon irradiation complex organic solids with strong UV absorption in the 2000 Å region (*45*). Destruction of NH_3 by reaction with OH (*9*) should also be greatly reduced, because photolysis of H_2O from photons with $\lambda < 2400$ Å will be suppressed. Submicrometer aerosols should settle out of the stratosphere on time scales $t \simeq$ 0.5 to 3 years (*46*), fairly independent of the atmospheric pressure on early Earth; $t \simeq 1$ year applies to the present Earth ($p_s = 1$ bar, gravitational acceleration $g = 980$ cm s^{-2}) and Venus ($p_s = 90$ bar, $g = 890$ cm s^{-2}).

To calculate the prolongation by shielding of the ~10-year photodissociation time scales of unshielded NH_3, we must evaluate two photodestruction rates. The photodestruction rate in the absence of any shielding is $J = \int I_\lambda \sigma_\lambda d\lambda$, where I_λ is the solar flux at the top of the atmosphere (*47*) and σ_λ is the NH_3 absorption cross section (*9*). If a high-altitude UV shield of optical depth τ_λ is present, this rate becomes $J' = \int I_\lambda e^{-\tau_\lambda \sec\theta} \sigma_\lambda d\lambda$, where θ is the solar zenith angle; we take $\theta = 45°$, the mean angle. These integrals effectively extend only from 1100 to 2300 Å (Fig. 1), because the solar flux is negligible below 1100 Å and NH_3 absorption is negligible above 2300 Å. The ratio J/J' therefore gives the enhancement of the lifetime of atmospheric NH_3 in the presence of a UV shield of optical depth τ_λ. Because σ_λ is increasing steeply and the Planck function is decreasing steeply at 2000 Å, these integrals are given approximately by their values near 2000 Å. Before performing the full numerical integrations, we first examine such an approximation.

All organic solids strongly absorb at $\lambda <$ 2300 Å. The optical depth is given by $\tau_\lambda =$

$\phi_\gamma t\alpha_\lambda/4\pi\rho R^2$, where ϕ_γ is the production flux (mass per time) of UV-shielding organic solids, R is the planet's radius, ρ is the bulk density of the organic solids, $\alpha_\lambda = 4\pi k/\lambda$ is the linear absorption coefficient of the organic solids, and k is the imaginary part of the complex refractive index (Table 1). We choose a conservative value of $k(2000\ \text{Å}) \simeq 0.19$. The higher the proportion of elemental carbon, the higher k will be. We adopt $\rho \simeq 1.4$ to 1.6 g cm^{-3}, the range for the organic solids produced at low pressures from the radiation chemistry of 10:1 N_2-CH_4 gas mixtures (*48*).

Syntheses of organics in CH_4-N_2 models of Titan's atmosphere imply a production efficiency of 1.2×10^{-12} g erg^{-1} at $\lambda <$ 1550 Å (*49*). This value is within a factor of 2 of the photodissociation efficiency of CH_4 in pure CH_4 atmospheres at $\lambda \simeq 1295$ and 1470 Å (*50*). We calculate organic production efficiencies in UV-irradiated CH_4-NH_3 atmospheres (*51*) to be a factor of ~5 below those just cited for CH_4-N_2 atmospheres.

Most of the products of charged-particle irradiation of CH_4-N_2 atmospheres are in the form of organic heteropolymer (*52*). A lower limit on the fraction f of the irradiation products that are organic solids is taken to be 0.1 (*52*). We assume a similar range for the products of CH_4-N_2 photolysis. We estimate the net flux of UV energy below 1500 Å on Earth 4.0 Ga to have been 1×10^{27} erg year^{-1} (*11*, *53*), three times the current value. The production of high-altitude organic aerosols from CH_4 photolysis in the terrestrial atmosphere 4 Ga was then $\phi_\gamma \simeq (1.2 \times 10^{15})f$ g year^{-1}. Other sources of high-altitude organic aerosols (*11*) amount to $\lesssim 10^{13} f$ g year^{-1}.

This calculation assumes the production of organic aerosols to have been UV-limited. The contemporary carbon outgassing rate (mainly as CO_2) from mid-ocean ridges is 1×10^{13} to 1×10^{14} g year^{-1}; estimates (*54*) of outgassing rates 3 Ga range from 4×10^{13} to 6×10^{14} g year^{-1} (or ~10^{11} cm^{-2} s^{-1}). The outgassing rate 4 Ga must have been greater still but with an unknown CH_4/CO_2 ratio. It seems possible, even without exogenous input (*55*), that the carbon outgassing source would have been able to keep pace with the organic solid production sink, provided $CH_4/CO_2 \gtrsim 1$. Integrated over 1 billion years, the organic production would have been of the same order as the total estimated terrestrial inventory of carbon in the mantle and crust (*56*).

NH_3 Lifetimes, Diffusion Flux, and Resupply

Choosing $k(2000\ \text{Å}) = 0.19$, appropriate for kerogen, with $\rho = 1.6$ g cm^{-3}, $t = 1$ year, and $f = 0.5$, we find $\alpha_\lambda = 1.2 \times 10^5$ cm^{-1} and $\tau \simeq 8.8$, yielding an attenuation of NH_3 photolysis by a factor $\exp(-\tau \sec\theta) = 3.9 \times 10^{-6}$. The lifetime of $[NH_3] \sim 10^{-5}$, instead of 10 years, would then be 2.5×10^6 years. The rate of NH_3 photodestruction would be $\sim 2 \times 10^{10}$ g year^{-1} in this case or, integrated over 1 billion years, about 2×10^{19} g, or 0.5% the current atmospheric N_2 abundance. By comparison, the contemporary biogenic value is $\sim 10^{13}$ to 10^{14} g NH_3 year^{-1} (*9*, *31*, *57*). In CH_4-rich reducing atmospheres, NH_3 is also a degradation product of HCN; steady-state production is estimated at $\sim 10^{12 \pm 1}$ g NH_3 year^{-1} (*58*).

Models with $k(2000\ \text{Å}) = 0.22$, appropriate for N_2-CH_4 irradiation residues (Titan tholin), with $\rho = 1.4$ g cm^{-3}, $t = 1$ year, and $f = 0.5$ give $\tau \simeq 11.7$, or a $[NH_3] \sim 10^{-5}$ lifetime of 1.5×10^8 years. Averaging the values for kerogen and Titan tholin, the lifetime of a $[NH_3] \sim 10^{-5}$ primeval atmosphere as a function of f and sedimentation time t for $k(2000\ \text{Å}) \simeq 0.21$ and $\rho = 1.5$ g cm^{-3} shows that effective shielding of NH_3 by organic solids fails only for low t and low f (Table 2).

The full integrations of J/J' for kerogen optical constants, $\rho = 1.6$ g cm^{-3}, $t = 1$ year, and $f = 0.5$ give $J/J' = 1.0 \times 10^5$, or lifetimes for $[NH_3] \sim 10^{-5}$ only a factor of 2.5 less than those found by the 2000 Å approximation (Fig. 2). [The net solar UV flux 4 Ga for $\lambda < 2300$ Å was about the same as it is today (*11*, *53*).] For Titan tholin optical constants and $\rho = 1.4$ g cm^{-3}, the result is $J/J' = 9.6 \times 10^6$, or a lifetime of $\sim 10^8$ years. As a consistency check, we note that for many of the organic solids (Table 1), $\tau(5500\ \text{Å})/\tau(2000\ \text{Å}) \sim 0.1$ or less, so that even for $\tau(2000\ \text{Å}) \sim 10$, there is still enough sunlight reaching Earth's surface to drive a significant net greenhouse effect.

However, atmospheres in which NH_3 lifetimes are sufficiently prolonged will violate the assumption that NH_3 photolysis occurs below the organic aerosol shield. For example, for $f = 0.5$ and 1-year sedimentation times (Table 2), shielding lengthens NH_3 photolysis lifetimes by a factor $\sim 10^6$. In this case, the time scale for NH_3 to reach the altitude of CH_4 polymerization would be shorter than the photolysis lifetime, and the NH_3 would no longer be shielded. Then the required NH_3 resupply flux ϕ will be given by its flux, dominated by eddy diffusion (*59*), to the CH_4 polymerization altitude. Contemporary eddy diffusion constants K vary from $\sim 10^3$ cm^2 s^{-1} just above the tropopause to $\sim 10^6$ cm^2 s^{-1} at an altitude of 80 km (*60*). If we choose $K = 10^5$ cm^2 s^{-1} for the early atmosphere (*6*), and

Table 1. Values of the imaginary part of the complex refractive index k at 2000 Å for candidate organic solids that could serve as a UV shield.

Material	k_λ
Organic residue from irradiation of 6:1 H_2O:C_2H_6 ice mixture* (*67*)	0.17
Kerogen (*67*)	0.19
Organic residue from irradiation of 10:1 N_2:CH_4 gas mixture (*48*)	0.22
Organic residue from irradiation of H_2O-CO-CH_4-NH_3 ice mixture (*68*)	0.21 to 0.29
Organic refractory grains modeling interstellar dust (*69*)	~0.2
Organic refractory grains modeling cometary dust (*70*)	0.28
Elemental carbon (*71*)	0.39
Gas-phase–deposited amorphous C (*72*)	0.47
Hydrogenated amorphous C from C electrodes (*73*)	0.55
Hydrogenated amorphous C from benzene oxidation (*74*)	0.50
Arc-evaporated C (*75*)	0.65
CH_y heated to 500 K† (*76*)	0.82
Soot in hydrocarbon flames‡ (*77*)	~1.0

*Results are similar to those for 6:1 H_2O:CH_4 ice irradiation (*78*). †At 0.276 μm. ‡Estimated from dispersion relations at 300, 1000, and 1600 K at 0.3 μm; all curves are rising toward shorter wavelengths.

Table 2. Lifetimes for atmospheres with $[NH_3] \sim 10^{-5}$. The sedimentation times are from Oberbeck *et al.* (*46*). E indicates a value >4.5 billion years.

Sedimentation time (years)	Lifetime (years) for given fraction of irradiation products in organic solids		
	0.1	0.5	0.9
0.5	40	2×10^4	5×10^6
1	200	2×10^7	E
3	6×10^4	E	E

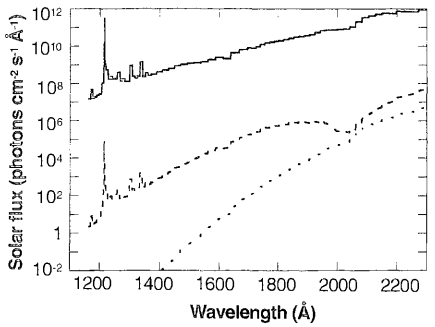

Fig. 2. Solar UV flux with no attenuation (heavy line), compared with the flux at Earth's surface in the presence of a high-altitude organic solid formed by reactions of UV light with CH_4. The dashed line shows the UV flux if the high-altitude haze is assigned kerogen optical constants. The dotted line shows the same, but with optical constants appropriate to Titan tholin.

an atmospheric scale height $H = 8.4$ km, an upper limit (*61*) for the NH_3 eddy diffusion flux is $\phi_e \approx (K/H)[NH_3]n(z) \approx 2 \times 10^9$ cm^{-2} s^{-1} or $\sim 10^{13}$ g year^{-1} at $z = 70$ km; here $n(z)$ is the contemporary atmospheric number density at altitude z. {Lower polymerization altitudes would give higher ϕ_e due to larger $n(z)$ [$n(z = 40$ km) $\sim 40n(z = 70$ km)], although this effect is mitigated by lower values of K at lower $n(z)$.} In this case, $[NH_3] \sim 10^{-5}$ has a lifetime of $\sim[NH_3]M_a/\phi \sim 5000$ years (where $M_a = 5 \times 10^{21}$ g is the mass of the contemporary atmosphere), so that the current inventory of N_2 would be generated by NH_3 photolysis in $\sim 5 \times 10^8$ years. Given resupply, half-billion-year time scales for the duration of $[NH_3] \sim 10^{-5}$ atmospheres appear possible.

Would CH_4 have been irreversibly converted to organic solids and NH_3 to N_2 and organic solids on the early Earth, or are there mechanisms for recycling? Tholins are stable and require temperatures of 600° to 1000°C for half their mass to be vaporized (*62*). If plate tectonics were in operation 4 Ga, with subduction of the crust down to hundreds of kilometers depth and a geothermal gradient substantially steeper than that which exists today, tholins may have been reprocessed into NH_3, CH_4, and other simple organic gases. Recycling of N_2 into NH_3 may occur by means of electrical discharges and NO (*30*) and TiO_2 photochemical catalysis in titanium-rich deserts (*63*). These processes reduce the need for outgassing or exogenous resupply. Because methanogens were among the earliest microorganisms, and life seems to have been widespread by 3.5 and possibly by 3.85 Ga (*18*), there is no need to seek nonbiological sources of CH_4 (or NH_3) in that period or later. Ultraviolet optical depths above 5 to 10 on Earth would have played an important role in shielding early organisms from UV damage (*64*).

A point of comparison for this model is provided by Saturn's moon Titan. The UV and radiation processing of Titan's N_2-CH_4 atmosphere produces an aerosol with average particle radii ~ 0.25 μm and an optical depth of about 7 between 2000 and 3000 Å (*65*), about the same as the optical depths calculated here for CH_4 photolysis in the early terrestrial atmosphere.

There are clearly uncertainties in many of the input parameters in our calculations. Nevertheless, were the atmosphere of the early Earth reducing, our results suggest that it would have been self-shielding against UV photodissociation. Were this atmosphere instead rich in N_2 with minor CO_2 and CH_4 components, self-shielding may also have been possible, but only if a CH_4/CO_2 ratio $\gtrsim 1$ could have been maintained. We wish only to suggest that a self-consistent solution to the early faint sun dilemma (*66*), without invoking massive CO_2 atmospheres, appears to be viable.

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Trichodesmium, a Globally Significant Marine Cyanobacterium

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Planktonic marine cyanobacteria of the genus *Trichodesmium* occur throughout the oligotrophic tropical and subtropical oceans. Their unusual adaptations, from the molecular to the macroscopic level, contribute to their ecological success and biogeochemical importance. *Trichodesmium* fixes nitrogen gas (N_2) under fully aerobic conditions while photosynthetically evolving oxygen. Its temporal pattern of N_2 fixation results from an endogenous daily cycle that confines N_2 fixation to daylight hours. *Trichodesmium* colonies provide a unique pelagic habitat that supports a complex assemblage of consortial organisms. These colonies often represent a large fraction of the plant biomass in tropical, oligotrophic waters and contribute substantially to primary production. N_2 fixation by *Trichodesmium* is likely a major input to the marine and global nitrogen cycle.

Trichodesmium, a colonial marine cyanobacterium (*1*) (Fig. 1), has intrigued naturalists, biologists, and mariners for well over a century (*2*). These cyanobacteria have been reported throughout the tropical and subtropical Atlantic, Pacific, and Indian oceans, as well as the Caribbean and South China seas (Fig. 2) (*3*, *4*). Modern interest in *Trichodesmium* dates to the early 1960s with the recognition that the biological productivity of large expanses of the ocean is often limited by the availability of nitrogen (*5*) and the observation that *Trichodesmium* is diazotrophic (that is, an N_2 fixer). The current focus in assessing the global role of the upper ocean in assimilating atmospheric CO_2 has elevated the importance of quantifying marine N_2 fixation.

Although major advances in understanding the biology of *Trichodesmium* have recently occurred on diverse fronts, several important questions remain largely unresolved: (i) Where does *Trichodesmium* fit in the broader scheme of cyanobacterial phylogeny? (ii) How does *Trichodesmium* sustain simultaneous photosynthetic O_2 evolution with nitrogenase activity, and why does it fix N_2 only during daylight periods? (iii) What physiological, morphological, and behavioral adaptations contribute to *Trichodesmium's* ecological success in the oligotrophic marine environment? (iv) What environmental and ecological factors control production and N_2 fixation in *Trichodesmium* in situ, and to what extent does it contribute to productivity, nutrient cycling, and trophodynamics in tropical and subtropical seas? (v) What is the over-

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