

Research Paper

A Revised, Hazy Methane Greenhouse for the Archean Earth

Jacob D. Haqq-Misra,^{1,3} Shawn D. Domagal-Goldman,^{2,3} Patrick J. Kasting,^{2,3} and James F. Kasting^{2,3}

Abstract

Geological and biological evidence suggests that Earth was warm during most of its early history, despite the fainter young Sun. Upper bounds on the atmospheric CO₂ concentration in the Late Archean/Paleoproterozoic (2.8–2.2 Ga) from paleosol data suggest that additional greenhouse gases must have been present. Methanogenic bacteria, which were arguably extant at that time, may have contributed to a high concentration of atmospheric CH₄, and previous calculations had indicated that a CH₄-CO₂-H₂O greenhouse could have produced warm Late Archean surface temperatures while still satisfying the paleosol constraints on pCO₂. Here, we revisit this conclusion. Correction of an error in the CH₄ absorption coefficients, combined with the predicted early onset of climatically cooling organic haze, suggest that the amount of greenhouse warming by CH₄ was more limited and that pCO₂ must therefore have been ≥ 0.03 bar, at or above the upper bound of the value obtained from paleosols. Enough warming from CH₄ remained in the Archean, however, to explain why Earth's climate cooled and became glacial when atmospheric O₂ levels rose in the Paleoproterozoic. Our new model also shows that greenhouse warming by higher hydrocarbon gases, especially ethane (C₂H₆), may have helped to keep the Late Archean Earth warm. Key Words: Archean—Methane—Early Earth—Hydrocarbons—Atmospheric gases. *Astrobiology* 8, 1127–1137.

Introduction

LIQUID WATER WAS PRESENT on the surface of Earth at least 3.5 billion years ago (Sagan and Mullen, 1972) and probably 4.4 billion years ago (Valley *et al.*, 2002), even though stellar evolution models predict that the Sun was 20–30% less luminous during Earth's early history. This has been termed the *faint young Sun paradox*. If the greenhouse effect on Earth was stronger during this early period, though, the paradox disappears. A dense CO₂ atmosphere (pCO₂ > 0.1 bar) could, in principle, have provided sufficient warming to keep Earth unfrozen (Kasting, 1987); however, constraints derived from Archean/Paleoproterozoic paleosols suggest that actual atmospheric CO₂ levels were not that high (Rye *et al.*, 1995; Sheldon, 2006). Because Earth's atmosphere contained very little O₂ during this time (Farquhar *et al.*, 2000), reduced gases could have been present at relatively high con-

centrations and may have provided additional greenhouse warming (Sagan and Mullen, 1972).

Methane is of particular interest because its photochemical lifetime is long in a low-oxygen atmosphere (Pavlov *et al.*, 2001) and because methanogenic bacteria could have produced a high biogenic CH₄ flux on early Earth (Kharecha *et al.*, 2005). Kiehl and Dickinson (1987) were the first to estimate quantitatively the greenhouse effect of CH₄ on early Earth. They calculated combinations of CO₂ and CH₄ required to maintain present-day global surface temperatures, given solar flux reductions of 5%, 15%, and 24%. Their model did not include absorption of visible and near-infrared solar radiation by CH₄, which becomes important at high CH₄ concentrations.

Pavlov *et al.* (2000) included these visible/near-infrared absorption bands of CH₄ in their climate model and performed a series of calculations, many of them focused on a

Departments of ¹Meteorology and ²Geosciences, The Pennsylvania State University, University Park, Pennsylvania.
³Penn State Astrobiology Research Center, The Pennsylvania State University, University Park, Pennsylvania.

time of 2.8 billion years before present (Ga), when the estimated solar luminosity was 80% of today's (Gough, 1981). They found that surface temperatures at or above the present mean value, 288 K, could have been maintained by a combination of ~ 1000 ppmv of CH_4 , along with 10–30 times the present atmospheric level (PAL) of CO_2 . Unfortunately, their calculations have recently been found to be in error. Because of a mistake regarding the numbering of spectral intervals, the strong $7.7 \mu\text{m}$ absorption band of CH_4 was inadvertently shifted longward by $\sim 2 \mu\text{m}$, which puts it right in the middle of the 8–12 μm "window region," where neither CO_2 nor H_2O absorbs strongly. (The error was discovered by comparison with other radiative transfer models—see the discussion below.) Hence, the Pavlov *et al.* (2000) climate model significantly overestimated the greenhouse effect of CH_4 .

Correcting and Testing the Methane Greenhouse Model

In testing our climate model and finding the mistake mentioned above, we compared our model with the radiative

transfer models RRTM (Mlawer *et al.*, 1997) and LBLRTM (Clough *et al.*, 1992; Clough and Iacono, 1995), and also with the SMART model (Meadows and Crisp, 1996; Crisp 1997). SMART and LBLRTM are detailed line-by-line codes and should, in principle, be the most accurate calculation tools. RRTM is a fast, correlated- k code that has been carefully validated against LBLRTM. To compare the different models, we (and our colleagues at Atmospheric and Environmental Research, Inc., and the Jet Propulsion Laboratory) ran all 4 of them for different CO_2 and CH_4 concentrations, using a pressure-temperature profile taken from the 1976 US Standard Atmosphere midlatitude summer model. The results are shown in Fig. 1. Results shown for our model (PSU IR) are for the corrected model, in which the $7.7 \mu\text{m}$ CH_4 band has been moved to its proper location. Our old, incorrect results are also included in the figure for comparison.

Inspection of Fig. 1 reveals significant discrepancies between the various models, including the 2 line-by-line codes. These differences can arise from a number of factors, including computational techniques, assumptions made in calculating line strengths and widths, the number of absorption

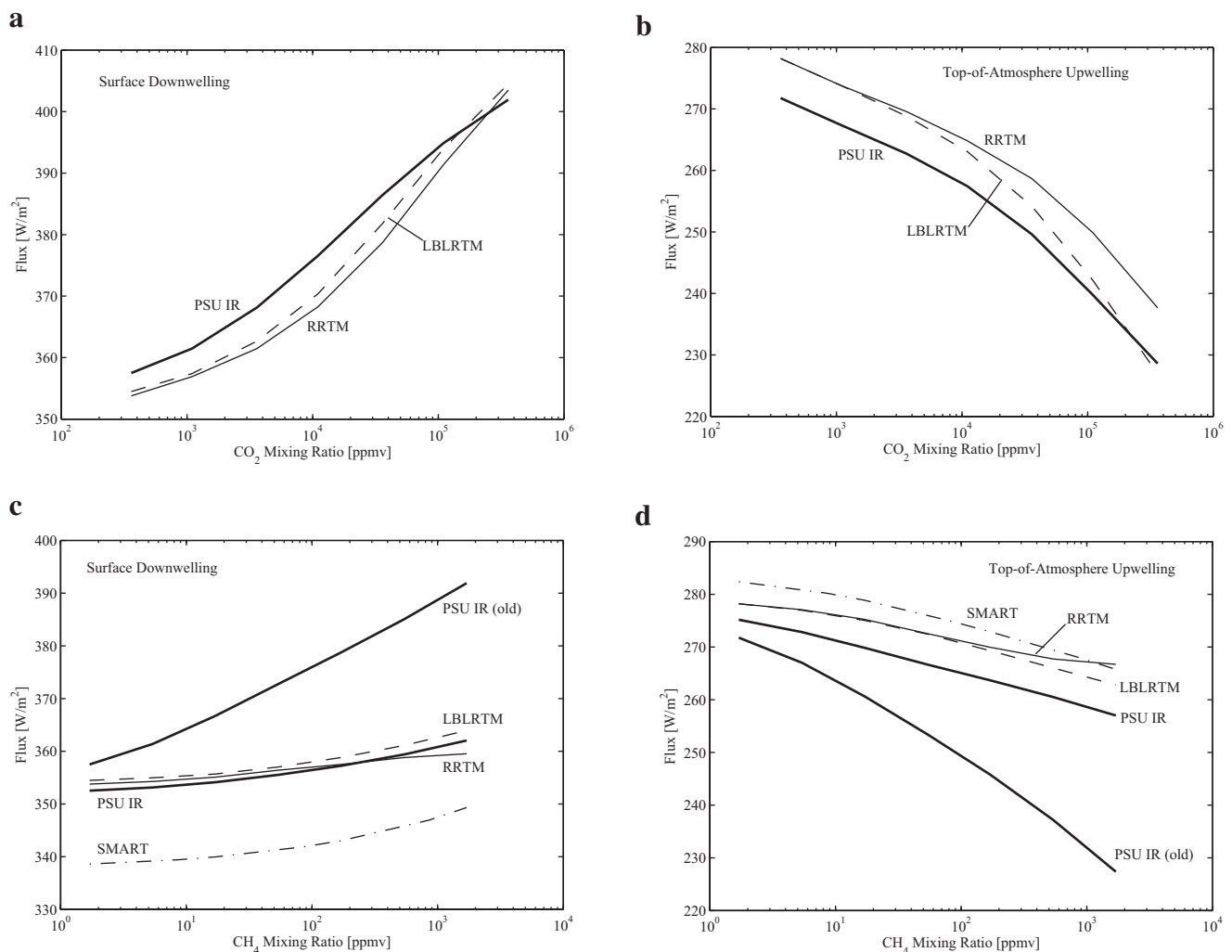


FIG. 1. Radiative flux comparisons for (a) surface downwelling and (b) top-of-atmosphere upwelling at constant CH_4 (1.7 ppmv), and (c) surface downwelling and (d) top-of-atmosphere upwelling at constant CO_2 (360 ppmv). All calculations assume a midlatitude summer (MLS) atmospheric profile.

bands considered, and, perhaps most importantly, the treatment of H₂O “continuum” absorption in the 8–12 μm window region. It is not our goal here to sort out all these inconsistencies. For our purposes, the *slopes* of the various curves for different CO₂ and CH₄ concentrations are the most important, as it is the slope of the curve that indicates the amount of infrared (IR) absorption by each individual gas. As can be seen in Fig. 1, the slopes are generally comparable, both for outgoing IR radiation at the top of the atmosphere and for downwelling IR radiation at the surface. By contrast, our old, uncorrected greenhouse model exhibits a distinctly steeper slope with respect to CH₄, which is consistent with our realization that the greenhouse effect was being overestimated.

One can legitimately ask whether any of the “fast” greenhouse models that have been used to study early Earth actually provide definitive results, given that different radiative parameterizations still disagree in detail. Our answer to this question would be that there is always room for improvement, even in our present, corrected model. It should be borne in mind, though, that the way the model is used is to first “tune” it to present Earth (*i.e.*, to make sure that it reproduces the observed mean surface temperature and vertical temperature profile) and then apply it to early Earth. In doing so, absolute errors in the calculation (*e.g.*, vertical offsets in the curves shown in Fig. 1) should tend to cancel out. So, our estimates of the amount of greenhouse forcing needed to warm early Earth should be reasonably reliable even if modest errors in absorption coefficients still exist.

Having corrected the problem with CH₄ absorption, we used the new model to repeat the calculations shown in Fig. 5 of Pavlov *et al.* (2000). (The old calculations are not shown here.) These simulations were performed for a time of 2.8 Ga, when solar luminosity was ~80% of the present value. The solid curves in Fig. 2 show predicted mean global surface temperature and planetary albedo as a function of CO₂ partial pressure (pCO₂) and CH₄ volume mixing ratio (fCH₄). Comparison with the old calculations shows that much of the greenhouse warming by CH₄ has been lost. In particular, there is only a small, roughly triangular region in which

the mean surface temperature is above the freezing point of water and pCO₂ is below the limit set by the paleosol data of Rye *et al.* (1995).

We shall discuss the paleosol limit further below, as the curve shown in Fig. 2a and in Pavlov *et al.* (2000) may not be a strict upper limit. If we treat it as one for now, though, it will be immediately apparent that there are problems. The mean annual surface temperature in the allowed region never gets much above ~280 K, which is about 8 degrees cooler than today. A climate with a mean temperature this low should be glacial, yet there is no evidence for glaciation during most of the Archean. Furthermore, some of the region marked by the triangle may be inaccessible for other reasons. Both photochemical models (Pavlov *et al.*, 2001) and laboratory experiments (Trainer *et al.*, 2004, 2006) have shown that organic haze should form in abundance when the atmospheric CH₄/CO₂ ratio exceeds ~1. For the 1-bar atmospheres considered here, this happens when fCH₄ > pCO₂. Experimentally, a thin haze may even begin to form at a C/O ratio of 0.6, which corresponds to a CH₄/CO₂ ratio of ~0.2 (Trainer *et al.*, 2004). The presence of organic haze produces an anti-greenhouse effect that cools the surface (McKay *et al.*, 1991; Pavlov *et al.*, 2001). When these effects are considered, it becomes difficult to argue that the CH₄-CO₂-H₂O greenhouse illustrated in Fig. 2 is consistent with a typically ice-free Late Archean climate.

Greenhouse Warming by C₂H₆

(i) Ethane photochemistry

The proposed CO₂ and CH₄ concentrations presented here are able to keep early Earth above freezing, but given the constraints discussed above, the modeled climate is still not consistent with the geological evidence. If the Late Archean climate was nonglacial, as seems likely, then mean annual surface temperatures must have been as warm as today (288 K), or warmer (Kiehl and Dickinson, 1987; Pavlov *et al.*, 2000), which suggests that still more greenhouse gases were present in the atmosphere. Indeed, Knauth and Lowe (2003) proposed that the Archean climate was hot (60–70°C) through-

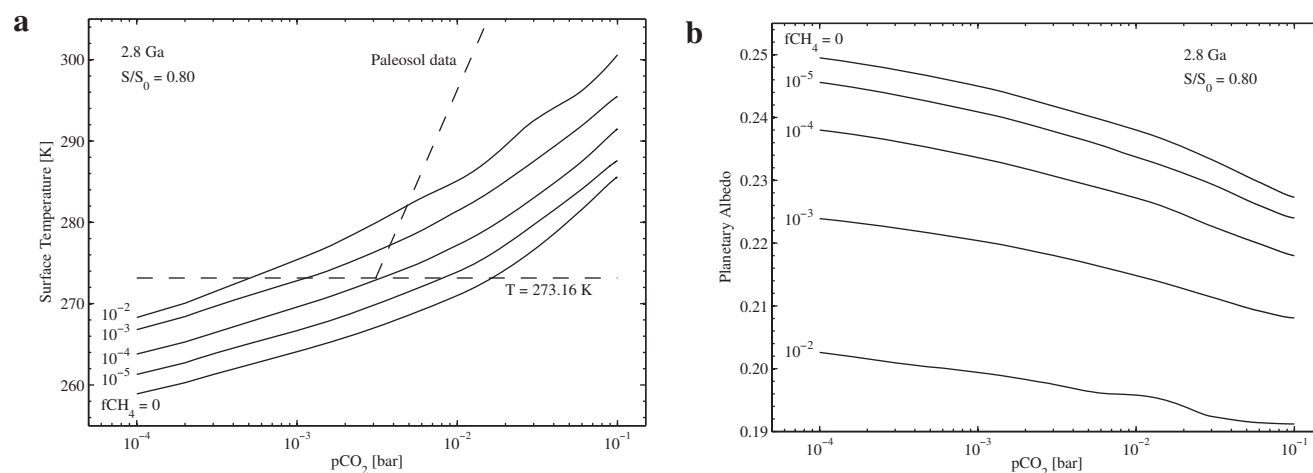


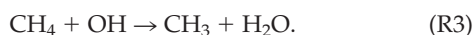
FIG. 2. (a) Calculated surface temperatures and (b) planetary albedos as a function of pCO₂ and fCH₄. The assumed solar luminosity is 80% of the present value ($S/S_0 = 0.80$). The greenhouse gases included in the calculation are CO₂, CH₄, and H₂O.

out the Archean and early Proterozoic, based on oxygen isotopes in ancient cherts. Other explanations for the isotope data are possible, however (Kasting *et al.*, 2006), so here we make the conservative assumption that the Late Archean climate was warm but not hot.

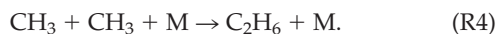
Hence, before calculating the cooling effects of the organic haze, we would like to first determine whether other gases might provide additional warming. Given the presence of significant concentrations of CH₄ and an abundance of solar ultraviolet radiation, higher hydrocarbon gases are likely candidates. Among these gases, ethane (C₂H₆) is the first to form and is generally the most abundant in model calculations (Kasting *et al.*, 1983; Zahnle, 1986; Pavlov *et al.*, 2001). Ethane forms in the following way. First, CH₄ is broken apart either by photolysis at extreme ultraviolet wavelengths ($\lambda < 145$ nm),



or by reaction with OH produced from H₂O photolysis at longer UV wavelengths ($\lambda < 240$ nm):



In a low-O₂ atmosphere, the methyl radicals that are formed can react with each other via the rapid 3-body reaction



By contrast, in today's high-O₂ atmosphere, CH₃ combines with O₂ to form the methylperoxy radical, CH₃O₂.

Ethane formed in low-O₂ atmospheres can undergo further reactions that result in the formation of other saturated and unsaturated hydrocarbons. Photolysis of C₂H₆ generates ethylene (C₂H₄) and acetylene (C₂H₂), whereas reaction of C₂H₆ with OH yields C₂H₅ radicals that can recombine with each other and with CH₃ to form propane (C₃H₈) and butane (C₄H₁₀). All these gases, except for acetylene, are effective greenhouse gases. However, they are less abundant than ethane; and, as we discuss below, their appearance at significant concentrations is accompanied by extensive organic haze formation. Hence, we ignore warming by these higher hydrocarbons for now and concentrate our efforts on the greenhouse effect of ethane.

We used an atmospheric photochemistry model descended from Pavlov *et al.* (2001) and Kharecha *et al.* (2005) to estimate ethane abundances in the anoxic Archean atmosphere as a function of CH₄ and CO₂ concentrations. Calculated C₂H₆ mixing ratios ranged from 10⁻⁴ ppmv to 100 ppmv over the range of atmospheres studied (Table 1). As one typical example, when the CO₂ and CH₄ mixing ratios

TABLE 1. C₂H₆ MIXING RATIOS PREDICTED BY THE PHOTOCHEMICAL MODEL AT SPECIFIED CO₂ AND CH₄ LEVELS

	$f\text{CH}_4 = 10$	100	1000	10,000
$f\text{CO}_2 = 100$	1.13×10^{-4}	0.158	3.77	103
1000	1.15×10^{-4}	0.0835	4.16	26.6
10000	1.67×10^{-3}	0.0359	0.425	9.88
10,0000	5.54×10^{-4}	0.0259	0.559	5.22

All values are ppmv.

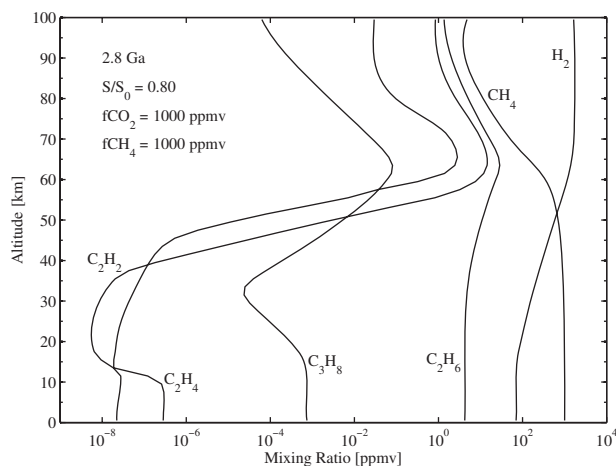


FIG. 3. Calculated altitude profiles for CH₄, C₂H₆, and other hydrocarbons for a 1-bar atmosphere with $f\text{CO}_2 = 1000$ ppmv and $f\text{CH}_4 = 1000$ ppmv.

are both equal to 1000 ppmv, C₂H₆ concentrations are predicted to be $\sim 4 \times 10^{-6}$, or 4 ppmv. Figure 3 shows calculated vertical profiles of hydrocarbon species for this particular CO₂/CH₄ combination. Methane and ethane have relatively constant mixing ratios up to an altitude of ~ 60 km, and they are more abundant than other hydrocarbons by several orders of magnitude. Both gases remain well mixed throughout the lower atmosphere in all these simulations. This is because ethane, like methane, has a short wavelength cutoff for UV photolysis and, hence, has a long photochemical lifetime. An Archean lifetime of $\sim 10,000$ years is typical for both gases.

(ii) Absorption of thermal infrared radiation by C₂H₆

We obtained thermal-infrared absorption coefficients for C₂H₆ from the Pacific Northwest National Laboratory database, which is accessible through the website of the NASA Astrobiology-affiliated Virtual Planetary Laboratory (<http://vpl.astro.washington.edu>). Ethane has a strong absorption band between 11 μm and 13 μm , as shown in Fig. 4. This is within the atmospheric window region (roughly 8–13 μm) where H₂O and CO₂ do not absorb strongly. The dashed lines in Fig. 4 show the boundaries of the wavelength bins in the radiation scheme of our climate model, with the strongest C₂H₆ absorption occurring within the 11.5–12.5 μm bin. The scale on the figure is linear, though, and the band wings can become important at high C₂H₆ concentrations, as will be demonstrated below.

To include C₂H₆ absorption in our climate model, we used the correlated-*k* distribution method (Fu and Liou, 1992; Mlawer *et al.*, 1997; Kato *et al.*, 1999) to fit the (room-temperature) Pacific Northwest National Laboratory data. The correlated-*k* method is a technique for rapidly approximating radiative fluxes within a relatively broad spectral interval with accuracy comparable to that given by line-by-line radiative transfer models. The spectral absorption coefficient $k(\nu)$ varies irregularly with wavenumber, but rearranging these absorption coefficients in ascending order yields a smoothly varying function. This cumulative distribution

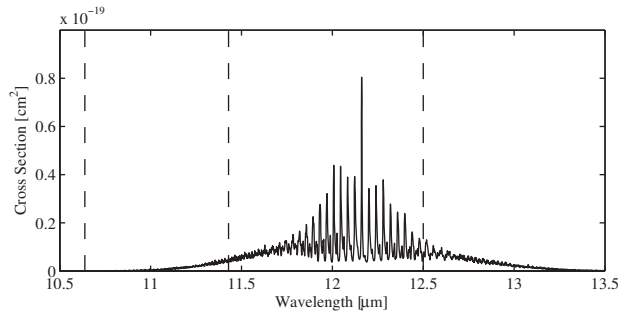


FIG. 4. Absorption cross sections for C_2H_6 in the atmospheric window region. Dashed lines indicate the boundaries of the wavelength bins in our climate model.

function g allows the absorption coefficients to be mapped from a spectral space to a space defined by g so that $k(\nu) \rightarrow k(g)$, where $g(k)$ is the fraction of absorption coefficients in the set less than k . Following Kato *et al.* (1999), 6 Gaussian quadrature points were selected in $g(k)$ to estimate a set of absorption coefficients for each wavelength interval. The transmission $T(u)$ through the atmosphere at a given model layer was then calculated as

$$T(u) = \sum_{j=1}^n a_j e^{-k(g_j)u}$$

where $k(g_j)$ is the absorption cross section at the quadrature point g_j , n is the number of quadrature points ($n = 6$ in this case), u is the amount of absorber over the path, and a_j is the Gaussian weight. The values of these Gaussian weights and absorption coefficients for C_2H_6 are shown in Table 2. A second C_2H_6 absorption band centered at $\sim 7 \mu m$ was also included in the model. The accuracy of this method is illustrated in Fig. 5, which compares the exact transmission calculation with the correlated- k coefficient approximation for the 11.5–12.5 μm wavelength bin. The fit is comparable to that of the CH_4 bands, which were also approximated with 6-term correlated- k sums.

To compute infrared fluxes in the wavelength intervals in which C_2H_6 absorbs, each of the six C_2H_6 k -coefficients was convolved with six k -coefficients for CH_4 , eight for CO_2 , and eight for H_2O , which required $6 \times 6 \times 8 \times 8 = 2304$ separate 2-stream radiative transfer calculations per spectral interval at each time step. Despite this added complexity, a typical calculation involving ~ 100 spectral intervals (solar and infrared) and several hundred time steps could still be performed in ~ 10 minutes on a 3.4 GHz, 64-bit Linux PC.

Other Changes to the Climate Model

The one-dimensional radiative-convective climate model used in these calculations is a direct descendent of the one used by Pavlov *et al.* (2000). The Archean atmosphere is assumed to have had a surface pressure of 1 bar and to have consisted mostly of N_2 , with variable concentrations of CO_2 , H_2O , CH_4 , and C_2H_6 . The assumption of a 1-bar atmosphere is consistent with the observation that N_2 is relatively inert and that most of Earth's nitrogen inventory resides in the atmosphere (Holland, 1978). All gases other than H_2O are considered to be well mixed in the model atmosphere, and O_2 and O_3 are assumed to be absent, as are clouds. A moist

adiabatic lapse rate is assumed in the model troposphere. The climate model is tuned to present Earth by assuming modern atmospheric composition and solar luminosity and then adjusting the surface albedo until the surface temperature stabilizes at 288 K (the observed global mean value). The surface albedo required to obtain this result is 0.219. This is higher than the actual surface albedo, and it therefore compensates for the absence of clouds in our model. Alternatively, one can view this as placing the cloud layer at the surface. As the Archean climate was at least as warm as today, and as cloud cover is generally a function of sea surface temperature, this tuning of the model seems reasonable. The calculated planetary albedos (Fig. 2b) are *lower* than Earth's actual planetary albedo (~ 0.3), as they must be in order to compensate for the lack of greenhouse warming by clouds.

TABLE 2. GAUSSIAN WEIGHTS AND ABSORPTION CORRELATED k -COEFFICIENTS FOR C_2H_6 IN THE LONGWAVE

Wavelength interval $\mu(m)$	Weights	Absorption coefficients (cm^{-2})
6.0606–6.4516	0.08566	3.1607×10^{-23}
	0.18038	7.4713×10^{-23}
	0.23396	2.2452×10^{-22}
	0.23396	9.2931×10^{-22}
	0.18038	3.0558×10^{-21}
	0.08566	5.7388×10^{-21}
6.4516–6.8966	0.08566	6.0680×10^{-21}
	0.18038	9.5224×10^{-21}
	0.23396	1.3251×10^{-20}
	0.23396	1.6683×10^{-20}
	0.18038	2.1862×10^{-20}
	0.08566	4.6329×10^{-20}
6.8966–7.4074	0.08566	1.0934×10^{-21}
	0.18038	2.7999×10^{-21}
	0.23396	7.0277×10^{-21}
	0.23396	1.1359×10^{-20}
	0.18038	1.5960×10^{-20}
	0.08566	2.1332×10^{-20}
7.4074–7.8431	0.08566	3.0909×10^{-24}
	0.18038	1.5773×10^{-23}
	0.23396	4.9806×10^{-23}
	0.23396	1.3673×10^{-22}
	0.18038	3.3965×10^{-22}
	0.08566	8.2701×10^{-22}
10.6383–11.4286	0.08566	2.3159×10^{-23}
	0.18038	8.6746×10^{-23}
	0.23396	2.6336×10^{-22}
	0.23396	9.1975×10^{-22}
	0.18038	2.3556×10^{-21}
	0.08566	3.9631×10^{-21}
11.4286–12.5000	0.08566	4.1940×10^{-21}
	0.18038	5.3313×10^{-21}
	0.23396	70534×10^{-21}
	0.23396	9.2389×10^{-21}
	0.18038	1.3508×10^{-20}
	0.08566	2.7746×10^{-20}
12.5000–13.8889	0.08566	1.0140×10^{-23}
	0.18038	6.6404×10^{-23}
	0.23396	4.4811×10^{-22}
	0.23396	2.2630×10^{-21}
	0.18038	5.1880×10^{-21}
	0.08566	7.8162×10^{-21}

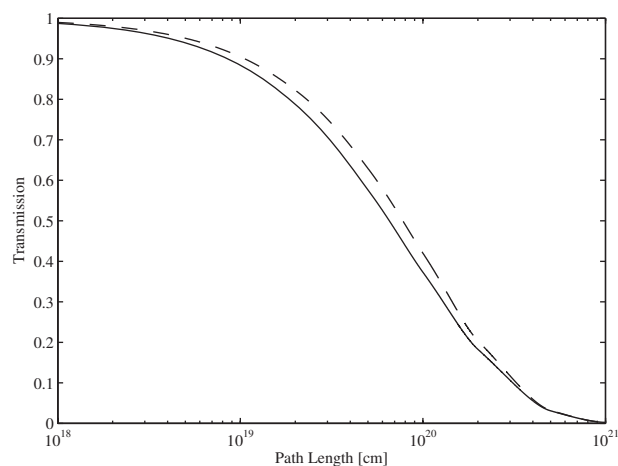


FIG. 5. Transmission as a function of path length for C_2H_6 . The solid curve is the calculated transmission, and the dashed curve shows the correlated- k approximation.

In addition to correcting the CH_4 absorption coefficients in the thermal infrared and adding absorption by C_2H_6 , we also modified the parameterization of CH_4 absorption in the near infrared. In the Pavlov *et al.* (2000) climate model, near-IR absorption at wavelengths between $1.07 \mu m$ and $4.54 \mu m$ was parameterized with use of 4-term exponential sum coefficients based on data from Strong *et al.* (1993). In that model, the pressure (P) dependence of the absorption coefficients was parameterized by including a factor, P^x , which multiplied the CH_4 path length. Detailed testing of this parameterization showed that it was inaccurate at low pressures, so we generated 4-term k -coefficient fits at 5 different pressures. Instead of starting from Strong's data, which were cast in the form of band models, we started from the 10-term exponential sum fits of Irwin *et al.* (1996). These fits were done on a relatively high-resolution spectral grid (10 cm^{-1}). We took these high-resolution k 's and used them as input for the 4-term, broadband, k -coefficient parameterization used in the climate model. The largest chi-squared value for the fits was 2.4×10^{-4} .

Results

Mixing ratios of atmospheric C_2H_6 as a function of CO_2 and CH_4 concentrations were already given in Table 1. Figure 6 shows the dependence of C_2H_6 concentration and several other higher hydrocarbons on the CH_4/CO_2 ratio for a fixed CO_2 level of 1000 ppmv. Given maximum C_2H_6 absorption coefficients of $\sim 3 \times 10^{-20} \text{ cm}^2/\text{molecule}$ (Table 2) and a total atmospheric column depth of $\sim 2 \times 10^{25} \text{ molecules/cm}^2$, parts of the window region reach optical depth unity at a C_2H_6 concentration of $\sim 2 \times 10^{-6}$, or 2 ppmv. This C_2H_6 concentration is reached at a CH_4/CO_2 ratio of approximately unity (Fig. 6). A CH_4/CO_2 ratio of unity is also the value at which the organic haze becomes optically thick (Zahnle, 1986; Pavlov *et al.*, 2001), so one may expect that the warming from the ethane will be offset by cooling from the haze.

Neglecting the haze for now, we show the greenhouse warming effect of increasing C_2H_6 at constant CO_2 (300

ppmv) in Fig. 7. At low CH_4/CO_2 ratios, the C_2H_6 concentration is too small to make much difference, but as this ratio reaches ~ 0.5 , the C_2H_6 mixing ratio increases to ~ 0.3 ppmv and begins to have an appreciable greenhouse effect. Just 1 ppmv of C_2H_6 increases the surface temperature by 3 degrees, and 10 ppmv warms the surface by about 10 degrees. The reason can be seen by looking back at Table 2 and Fig. 6. At 10 ppmv, the presence of C_2H_6 causes the atmosphere to reach optical depth unity down to a cross section of $\sim 5 \times 10^{-21} \text{ cm}^2/\text{molecule}$; hence, it blankets the window region from at least 11–13 μm .

With the greenhouse effect of C_2H_6 appropriately quantified, we repeated the calculations shown in Fig. 2 but with C_2H_6 included. The results are shown in Fig. 8. Calculated surface temperatures are substantially higher, particularly at low CO_2 partial pressures. The reason is that ethane concentrations are highest at low pCO_2 and high fCH_4 . Not all the parameter space shown in Fig. 8 would actually be accessible, however, because organic haze should form within the upper left-hand corner of this diagram.

We next carried out a series of climate calculations with the organic haze explicitly included. Particle output files from the photochemical model, which included particle size and number density as a function of altitude, were used as inputs for the climate model. (The photochemical model assumes a monodisperse particle size distribution, meaning that there is one particle size at each altitude.) Optical properties for the haze, including the extinction cross section (Q_{ext}), single scattering albedo (ω_0), and asymmetry factor (g), were calculated at each wavelength from tables computed by Pavlov *et al.* (2001). Those authors performed Mie scattering calculations at different particle size/wavelength ratios for particles with optical constants similar to those of Titan tholins.

As one example of the results, Fig. 9 shows calculated surface temperatures at a CO_2 partial pressure of 0.05 bar, with and without the effects of organic haze. The haze extinction optical depth in the mid-visible (500 nm) is also shown. The results are plotted on a linear axis because the cooling from the haze proceeds rapidly above an optical depth of ~ 0.2 . A

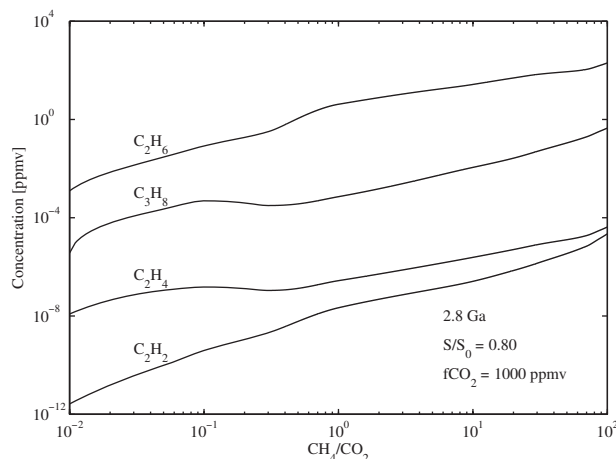


FIG. 6. Calculated hydrocarbon concentrations as a function of fCH_4 for an atmosphere containing 1000 ppmv CO_2 .

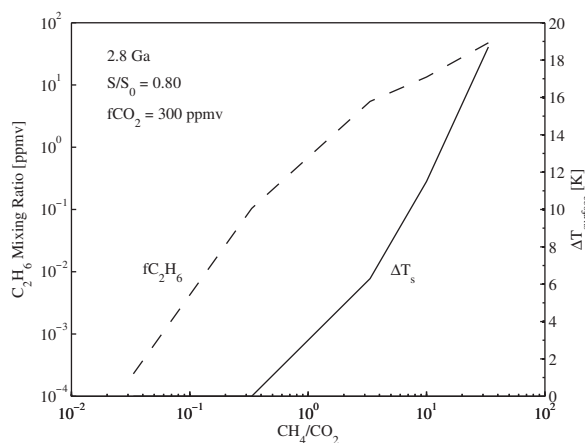


FIG. 7. Calculated C_2H_6 concentration (dashed curve) and ΔT_s (solid curve) as a function of CH_4/CO_2 ratio at $fCO_2 = 300$ ppmv. ΔT_s represents the difference in calculated surface temperature resulting from the inclusion of C_2H_6 .

region of optically thin haze exists at CH_4/CO_2 ratios of ~ 0.1 to 0.2 , and the calculated surface temperature peaks in this region. At still higher CH_4/CO_2 ratios, the haze builds quickly and causes surface temperatures to drop well below the freezing point of water.

Similar climate calculations, with haze included, were repeated for all combinations of CH_4 and CO_2 used in Figs. 2 and 8. The results are shown in Fig. 10. As in the haze-free case, the temperatures computed at low CH_4 concentrations do not change much because neither C_2H_6 nor haze is present in appreciable amounts. When the CH_4 abundance is larger than that of CO_2 , though, the formation of organic haze leads to a drastic cooling effect, which causes temperatures to drop well below freezing. Indeed, calculated surface temperatures start to decline even before this point is reached. The onset of significant haze formation and cooling in our model occurs when $CH_4/CO_2 \sim 0.1$. This value may be compared with the CH_4/CO_2 ratio of 0.2 reported by Trainer *et al.* (2004) for formation of measurable amounts of haze in their laboratory experiments.

Warm solutions, with surface temperatures at or above that of today (288 K), still can be identified in Fig. 10, but they require higher CO_2 partial pressures than indicated by the dashed curve marked "paleosol data." Warm, nonglacial solutions generally require $pCO_2 = 0.03$ bar, or 100 PAL. The same data are displayed as a contour plot of surface temperature versus CO_2 and CH_4 concentration in Fig. 11. Warm, ice-free Archean solutions occur in the upper right-hand corner of this figure, which correspond to hot (orange to red) colors. We have enclosed this region of this figure with a dashed line. Atmospheres that have a composition in the lower part of the region are consistent with a peak in the preservation of mass-independent sulfur isotope fractionation during the late Archean (Domagal-Goldman *et al.*, 2008). Note that the entire region is above the hard limit of Rye *et al.* (1995), ~ 0.03 bar CO_2 , marked in Fig. 11 by an arrow at -1.52 $\log(pCO_2)$.

Discussion

(i) The paleosol constraint on pCO_2

Despite the inclusion of C_2H_6 in our climate model, surface temperatures estimated for the Late Archean are substantially lower than those generated by the previous (and incorrect) Pavlov *et al.* (2000) model over much of the modeled range of atmospheric CH_4 and CO_2 concentrations. The new model still shows that a CH_4 concentration of ~ 1000 ppmv for this time period (Kharecha *et al.*, 2005) should have had a substantial warming effect (~ 10 K or more). The Kharecha *et al.* (2005) estimate for CH_4 production uses a detailed photochemical model combined with a diffusive gas transfer model for atmosphere-ocean exchange to estimate CH_4 release to the atmosphere. Because their calculation assumes the complete absence of oxygenic photosynthesis, we take the predicted ~ 1000 ppmv CH_4 concentration as a lower limit for the Late Archean. However, the CO_2 concentration required to supplement the warming by CH_4 and keep the climate from being glacial is significantly higher than estimated by Pavlov *et al.* (2000) and may be in conflict with the paleosol upper limit estimated by Rye *et al.* (1995).

The paleosol constraint plotted in Fig. 10 deserves further discussion, as it is not a hard-and-fast limit. In the first place, it is based on the *absence* of a particular mineral, siderite ($FeCO_3$), in soils, rather than on a mineral assemblage that was actually observed. Although the authors argue convincingly that siderite should have been present if pCO_2 were sufficiently high, an argument based on the lack of evidence is not inherently strong. Second, the paleolatitudes of the ancient soil samples that were studied are not known. The limit shown by the dashed curve in Fig. 10 implicitly assumes that the soils formed at the global mean surface temperature and hence at midlatitudes, but this need not have been the case. If the soils formed near the equator where temperatures were higher than the global average, then the relevant equilibrium constants in the siderite-iron silicate system would have been different, and the derived upper

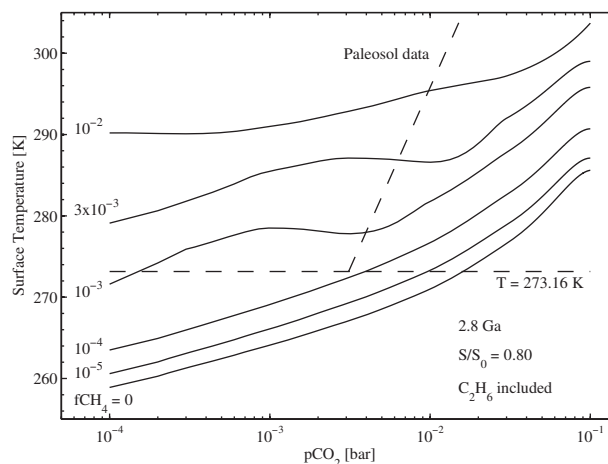


FIG. 8. Surface temperature as a function of pCO_2 and fCH_4 , with C_2H_6 included. Other parameters are the same as in Fig. 2. The mixing ratio of C_2H_6 is a function of both pCO_2 and fCH_4 , and was calculated with our photochemical model. Numerical values for fC_2H_6 are given in Table 1.

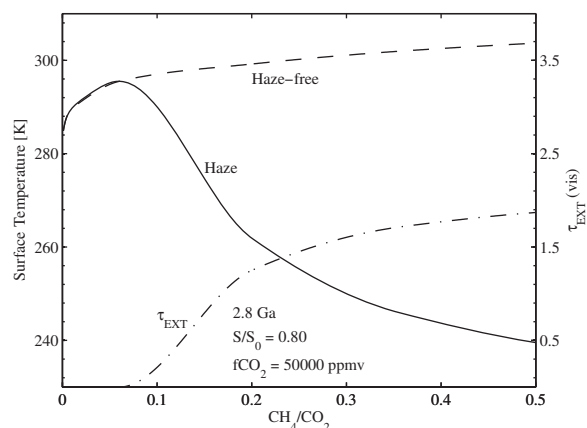


FIG. 9. Surface temperature and optical depth with increasing CH_4 at a CO_2 mixing ratio of 50,000 ppmv. The solid curve includes the effects of organic haze; the dashed curve is for a haze-free atmosphere. The dash-dot curve shows the extinction optical depth of the haze at 500 nm (mid-visible).

limit on $p\text{CO}_2$ could have been higher. Indeed, Rye *et al.* (1995) analyzed this possibility explicitly and suggested that the “hard” upper limit on $p\text{CO}_2$ in the Late Archean was about 0.03 bar, or ~ 100 PAL. This value is indicated in Fig. 10 by a downward-pointing arrow.

If one adopts this more generous paleosol constraint, it becomes much easier to generate warm, ice-free solutions. A combination of 0.03 bar of CO_2 and 3000 ppmv of CH_4 will produce a mean surface temperature of ~ 290 K, which might be nonglacial, depending on factors such as the positions of the continents. If one goes even further and ignores the “hard” paleosol limit, then achieving a warm Archean climate is not a problem. For example, a CO_2 partial pressure of 0.05 bar combined with a CH_4 mixing ratio of 1000 ppmv or more would create mean annual surface temperatures of 293 K or greater. This is the critical temperature for initiation of polar glaciation estimated by Kasting (1987) on the basis of the more recent climate record. [Based on oxygen isotope data, Antarctica started to become glaciated around 30 Ma, when global surface temperatures were about 5 degrees warmer than today (Miller *et al.*, 1987).] Interestingly, high CO_2 partial pressures also favor greenhouse warming by C_2H_6 ; increasing $p\text{CO}_2$ at a given CH_4/CO_2 ratio results in a higher C_2H_6 mixing ratio because the ethane concentration is a function of CH_4 abundance (Table 1).

One reason for suspecting that $p\text{CO}_2$ was relatively high during the Late Archean comes from analysis of siderite-facies banded iron formations that were formed during this same time interval (Ohmoto *et al.*, 2004). According to these authors, 100 PAL is an approximate lower limit on $p\text{CO}_2$ required to form the siderite banded iron formations. This limit is also not secure, as the effective CO_2 partial pressure in deep water may have been higher than in surface waters (or the atmosphere), as it is today (Kasting, 2004). Furthermore, other banded-iron formation facies include various iron silicates, such as greenalite, minnesotaite, and stilpnomelane (Holland, 1984), that should not have formed if $p\text{CO}_2$ were too high. These iron silicate minerals are often found in close association with siderite and magnetite (Klein and Beukes,

1992), which suggests that the primary mineral assemblage may have changed in response to fluctuations in local redox state. The fact that both iron silicates and iron carbonates are seen suggests that $p\text{CO}_2$ was somewhere near the boundary between these phases, *i.e.*, approximately ~ 0.03 bar, or 100 PAL.

(ii) Stability of hazy and haze-free Archean atmospheres

Elsewhere (Domagal-Goldman *et al.*, 2008), we have pointed out that hazy and haze-free atmospheres may have existed at different times during the Archean, a suggestion made previously by Sagan and Chyba (1997). Which type of atmosphere should actually have existed depends on both the biological productivity of the Archean ecosystem and the feedback loop between methane production and surface temperature. Methane production is thought to have been particularly high during the time period between the origin of oxygenic photosynthesis and the rise of atmospheric O_2 , nominally 2.7–2.4 Ga. This date for the rise of oxygen is based on the presence of 2- α methyl hopanes and sterols at the earlier date (Summons *et al.*, 1999; Brocks *et al.*, 1999) and the disappearance of sulfur mass-independent isotope fractionation at the latter (Farquhar *et al.*, 2000). (Oxygenic photosynthesis could have been invented earlier than 2.7 Ga, but there is no convincing evidence of this.) The reason for high methane production at this time is twofold (Catling *et al.*, 2001): (1) Biological productivity should have increased dramatically once oxygenic photosynthesis was invented (see, *e.g.*, Des Marais, 1997) and (2) in such an anoxic, low-sulfate environment (Canfield *et al.*, 2000), much of the organic matter that was created probably decayed by fermentation and methanogenesis.

The expected high production of CH_4 during the Late Archean could have had a significant influence on climate. As illustrated in Fig. 9, once CH_4 became an important contributor to the greenhouse effect, the Archean climate should have become highly sensitive to the CH_4/CO_2 ratio. If this ratio had been too high, then the haze would have been thick, which would have potentially led to a globally glaciated

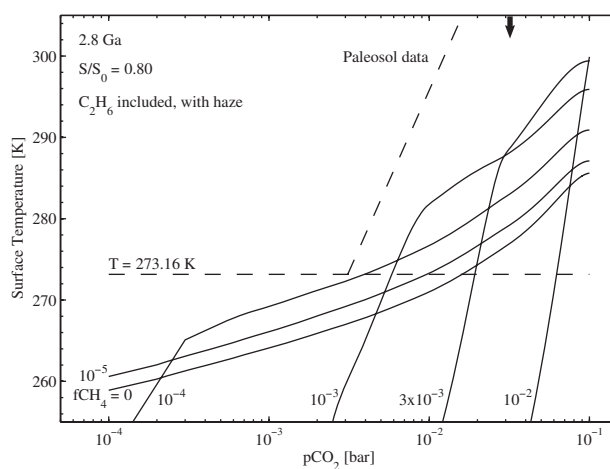


FIG. 10. Surface temperature with the effects of organic haze included. Other parameters are the same as in Fig. 8. The arrow indicates 100 PAL CO_2 , the hard limit based on paleosol interpretation.

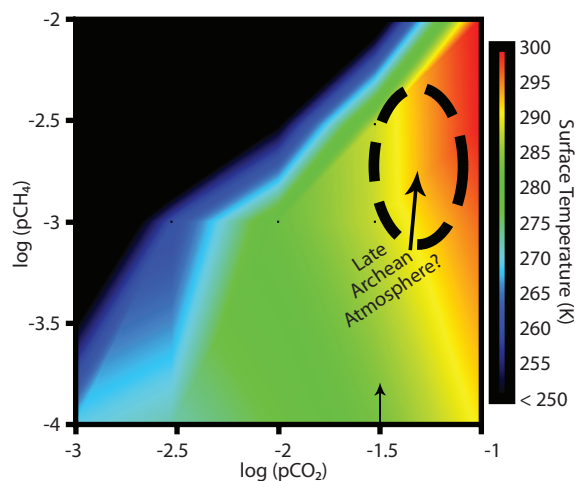


FIG. 11. Surface temperature contours plotted against $\log(p\text{CO}_2)$ and $\log(p\text{CH}_4)$. Black areas indicate surface temperatures below 250 K, grading into blue, cyan, green, yellow, orange, and red as temperature increases to 300 K. Regions of the diagram associated with glacier-free conditions ($> \sim 293$ K) are colored orange or warmer, and the “hard paleosol limit” on $p\text{CO}_2$ (Rye *et al.*, 1995) is represented by a vertical arrow at $\log(p\text{CO}_2) \sim -1.52$. The dashed oval represents atmospheric compositions that best recreate late Archean paleosol and glacial data. Black dots indicate the individual model results used to generate the contour plot.

state. This would have killed off most of the photosynthetic primary producers, as well as limited the transfer of H_2 and CH_4 between the atmosphere and the ocean; so, CH_4 production by the Archean biosphere should have increased with temperature if surface temperatures were comparable to or slightly higher than today’s. This relationship might not hold at the high surface temperatures predicted by Knauth and Lowe (2003), but we are discounting that possibility, as mentioned earlier. If temperatures were comparable to today’s, then cooling would have caused increases in glaciation, and CH_4 production would have increased with increasing temperature.

All of this points to the existence of a negative feedback loop, in which CH_4 production increases with surface temperature and surface temperature decreases with increasing CH_4 . This stabilizing feedback loop would only have existed if a thin haze were present. If the atmosphere were haze free, surface temperature would increase with increasing CH_4 , and the feedback loop would be positive (and, hence, unstable). This argument suggests that the Late Archean climate system should have stabilized in the regime where an optically thin organic haze was present. Such an atmosphere would also get the maximum possible warming out of CH_4 and C_2H_6 and, hence, would allow the lowest possible value of $p\text{CO}_2$.

(iii) How robust is the hazy greenhouse solution?

If our new calculations are correct, then the methane greenhouse story for the Archean is more complicated than researchers, including us, have been assuming. The presence of methane in the early atmosphere could have either caused warming (through the greenhouse effect) or cooling (from

haze formation). Which of these dominates depends on a multiplicity of factors, the most important of which are (1) the photochemistry of haze formation, (2) the abundance and greenhouse effect of higher hydrocarbon gases, and (3) the number density, composition, size distribution, and shapes of haze particles formed at different CH_4/CO_2 ratios.

Our model yields only a few degrees of warming from higher hydrocarbons, represented here by C_2H_6 , because the haze starts to form just as C_2H_6 becomes abundant. But the chemical scheme for haze formation, from Pavlov *et al.* (2001), is admittedly incomplete. Methane polymerization is assumed to proceed by way of polyacetylenes, based largely on the reaction mechanism of Yung *et al.* (1984), and the polymerization process is truncated at C_4 hydrocarbons. In other words, C_4 hydrocarbons are assumed to be converted directly into aerosol particles. In reality, at temperatures relevant to Earth’s atmosphere, particle condensation would likely not begin until carbon chains are much longer, C_{12} to C_{15} . Furthermore, if back reactions occur during the buildup to these chain lengths, then the actual rate of haze formation might be slower than predicted by our model.

Organic haze particles formed in Earth’s CO_2 rich early atmosphere should also have been partially oxygenated, unlike those found in Titan’s cold, nearly oxygen-free atmosphere. This could conceivably lower the real index of refraction of the particles, which would cause them to absorb less sunlight and thus reduce their anti-greenhouse effect. Measuring the optical properties of such particles in the laboratory could resolve this question. An improved model of the haze should also incorporate a more realistic particle size distribution at each altitude, as in Turco *et al.* (1979) for example, in place of the assumed monodisperse size distribution. Some combination of the factors just mentioned might have allowed for more greenhouse warming by C_2H_6 and possibly other hydrocarbon gases, before haze optical depths became significant.

Conclusions

A warm, ice-free Archean climate could have been maintained by greenhouse warming from CH_4 and C_2H_6 , in addition to CO_2 and H_2O . The absorption features of C_2H_6 in the 8–12 μm atmospheric window region make it an effective warming agent in an anoxic environment. However, cooling by organic haze becomes significant at CH_4/CO_2 ratios greater than a few tenths, which effectively limits the greenhouse warming that can be obtained by hydrocarbon gases. Hence, a warm Archean climate may require a CO_2 partial pressure of 0.03 bar or more, somewhat in excess of values predicted from analysis of paleosols.

A CH_4 concentration of ~ 1000 ppmv or greater could have been maintained during the Archean by an active methanogenic biota, which was sensitive to changes in surface temperature. Methane production should have peaked during the Late Archean, following the invention of oxygenic photosynthesis and the accompanying increase in primary productivity. During this time, the climate may have stabilized with a thin organic haze maintained by the negative link between haze thickness and temperature, coupled with the positive link between temperature and CH_4 production.

Despite the significantly smaller amount of greenhouse warming provided by CH_4 in this model compared with pre-

vious calculations, the idea that CH₄ was an important part of the Archean climate system remains intact. The rise of atmospheric O₂ at ~2.4 Ga could still have caused as much as 10 K of cooling and, thus, remains a plausible trigger for the glaciations that occurred at that time. Further progress in estimating the effects of CH₄ on Archean climate will require more detailed photochemical and microphysical modeling of hazy CH₄ rich atmospheres, a better understanding of the relationship between CH₄ production and Archean ecosystems, and stronger empirical constraints on atmospheric CO₂.

Note added in proof

Since this paper was accepted, a new study has been published (von Paris *et al.*, 2008) that suggests that greenhouse warming by CO₂ should have been substantially higher than predicted by previous calculations. If true, then perhaps pCO₂ could have been lower than the (original) paleosol limit and still have kept Earth warm, so additional greenhouse gases may not have been needed. The von Paris *et al.* (2008) study, though, compared the amount of CO₂ required to reach 273 K in their model with the amount needed to achieve 278 K, or even higher, in the Kasting (1987) model. (See their Fig. 11.) If one compares Case 2a in Table 4 of their model with Fig. 5 of Pavlov *et al.* (2000) or with Fig. 2a in this paper, one finds that all three models require pCO₂ = ~0.02 bar to keep the mean surface temperature above freezing for 0.8 times present solar luminosity and no CH₄. Hence, it appears that all three models obtain approximately the same amount of greenhouse warming from CO₂.

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Abbreviations

IR, infrared; PAL, present atmospheric level.

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Address reprint requests to:
Jacob D. Haqq-Misra
407 Walker Building
Pennsylvania State University
University Park, PA 16802

E-mail: misra@meteo.psu.edu