A COUPLED ECOSYSTEM-CLIMATE MODEL FOR PREDICTING THE METHANE CONCENTRATION IN THE ARCHEAN ATMOSPHERE

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Abstract. A simple coupled ecosystem-climate model is described that can predict levels of atmospheric CH_4, CO_2, and H_2 during the Late Archean, given observed constraints on Earth's surface temperature. We find that methanogenic bacteria should have converted most of the available atmospheric H_2 into CH_4, and that CH_4 may have been equal in importance to CO_2 as a greenhouse gas. Photolysis of this CH_4 may have produced a hydrocarbon smog layer that would have shielded the surface from solar UV radiation. Methanotrophic bacteria would have consumed some of the atmospheric CH_4, but they would have been incapable of reducing CH_4 to modern levels. The rise of O_2 around 2.3 Ga would have drastically reduced the atmospheric CH_4 concentration and may thereby have triggered the Huronian glaciation.

1. Introduction

A number of different arguments suggest that methane was an important trace constituent in Earth's primitive atmosphere. Data from paleosols (Rye *et al*., 1995) indicate that atmospheric CO_2 concentrations were too low to compensate for the estimated 20% reduction in solar luminosity at 2.8 Ga. CH_4 is a good absorber of infrared radiation and, hence, could have bolstered the atmospheric greenhouse effect and kept the early Earth from being frozen (Kiehl and Dickinson, 1987). Furthermore, the organisms that produce CH_4 today, methanogenic bacteria, are thought to have been amongst the earliest inhabitants of this planet. They represent early lineages in the Archaeal domain of the universal tree of life (Woese and Fox, 1977) and they utilize substrates that are thought to have been abundant on the early Earth. For example, all methanogens can use molecular hydrogen to reduce CO_2:

$$CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O. \tag{R1}$$

Some methanogens can also metabolize other carbon-containing compounds, such as acetate and formate, but the reaction above would probably have been the most important during the Archean because of the widespread availability of CO_2 and

H_2. As discussed further below, atmospheric CO_2 concentrations at that time could have ranged from the present level of $\sim 3 \times 10^{-4}$ atm up to over 1000 times that value. The predicted H_2 partial pressure in a weakly reducing primitive atmosphere is 10^{-4}-10^{-3} atm (Pinto *et al.*, 1980; Walker *et al.*, 1983; Kasting and Brown, 1998). This is a factor of 10–50 lower than the Michaelis-Menton K_m values for modern methanogens (Zinder, 1993, p. 143), but still well above the minimum threshold of 40 μatm at which methane can be produced in pure cultures (Kral *et al.*, 1998).

High concentrations of atmospheric methane are predicted only if the Archean atmosphere was essentially devoid of O_2. In today's oxidizing atmosphere, the photochemical lifetime of methane is just 12 yr. Thus, despite the presence of a substantial biological flux of ~ 500 Tg (CH_4) yr^{-2} (Watson *et al.*, 1990), the atmospheric CH_4 mixing ratio is only about 1.6 ppm. This is too low to produce significant greenhouse warming (see below). In an anoxic primitive atmosphere, however, photochemical model calculations indicate that the same methane source could have supported an atmospheric CH_4 mixing ratio on the order of 3×10^{-3}, or 3000 ppm (Zahnle, 1986; Kasting and Brown, 1998). The lifetime of methane under these circumstances is $\sim 20,000$ yr.

How long the primitive atmosphere remained anoxic is a matter of continued debate. Almost all authors agree that the prebiotic atmosphere was anoxic (Kasting, 1993, and references therein). Some authors (e.g., Holland, 1984, 1994) suggest that low concentrations of O_2, 10^{-4} PAL (times the Present Atmospheric Level) or more, were present throughout the Archean. Others (Ohmoto, 1996, 1997) think that pO_2 had already reached modern values by that time. The recent discovery of cyanobacterial and eukaryotic biomarkers in shales dated at 2.7 Ga (Brocks *et al.*, 1999) lends support to the idea that free O_2 was present in at least some environments. Other geologic evidence, though, including detrital uraninite and pyrite minerals, redbeds, banded iron-formations (Cloud, 1972; Walker *et al.*, 1983; Kasting, 1993), and sulfur isotope ratios (Canfield *et al.*, 2000) suggests that atmospheric pO_2 was extremely low prior to 2.0–2.4 Ga. The existence of eukaryotes could be explained by the presence of localized oxygen oases in high-productivity regions in the surface ocean (Kasting *et al.*, 1992). We include such regions as part of our model. We assume that atmospheric pO_2 was very low (10^{-6} atm or below) until at least 2.4 Ga. This interpretation is consistent with carbon isotopic evidence – specifically, the presence of very light kerogens in rocks dated at 2.8 Ga – that is most easily explained if methane was an abundant atmospheric constituent (Hayes, 1983, 1994).

A problem with the photochemical model predictions for Archean methane concentrations is that it is difficult to estimate how large the biological source of methane might have been at that time. Today, methane is produced in anaerobic environments such as the intestines of ruminants and the water-logged soils underlying rice paddies. On an anoxic early Earth, methanogens could have flourished in many different, more exposed environments; however, the overall level of bio-

logical productivity may have been much smaller. So, the actual biological source strength for methane during the Archean is difficult to determine.

Here, we offer a new estimate for the CH_4 concentration in the Archean atmosphere, based on climatic and thermodynamic considerations. The results, which were already anticipated by Kral *et al.* (1998), suggest that methane was indeed an abundant trace constituent and an important contributor to the atmospheric greenhouse effect. We note that Kral *et al.* were incorrect, however, in assuming that methanogenesis would be the sole loss process for hydrogen on a methanogen-dominated early Earth. Contrary to what they say, H_2 is produced photochemically at a prodigious rate in such an atmosphere, and so escape to space could have continued to be an important loss process for hydrogen even if methanogens had converted most of the H_2 into CH_4. Thus, one needs to balance the atmospheric hydrogen budget in order to predict how much H_2 would have been present.

2. A Coupled Ecosystem-Climate Model for the Late Archean

We describe here a coupled ecosystem/climate model intended to simulate the environment of the Late Archean, around 2.8 Ga. For simplicity, we begin by considering a homogeneous, anaerobic global ecosystem. We then modify the model by incorporating the high-productivity, and possibly O_2-rich, regions of the surface ocean mentioned above.

If the 2.8-Ga atmosphere was essentially anoxic, the two major greenhouse gases (besides water vapor, which acts as a feedback on climate) should have been CH_4 and CO_2. Using a one-dimensional, radiative-convective climate model (Pavlov *et al.*, 2000), we estimated the global mean surface temperature, T_s, as a function of the concentrations of these two gases. (Figure 1). The solar luminosity at 2.8 Ga is assumed to have been 80% of its present value (Gough, 1981). Acceptable solutions to the Archean climate problem lie in the upper left corner of the figure, where T_s exceeds the freezing point of water and pCO_2 is below the upper limit implied by the paleosol data. The actual surface temperature was probably higher than today's value (288 K), as indicated by the lack of evidence for glaciation at that time. CH_4 is a very good greenhouse gas: If the CH_4 mixing ratio, $f(CH_4)$, was higher than $\sim 10^{-4}$ (100 ppm), then surface temperatures above freezing are possible even if pCO_2 was no higher than today.

An analytic approximation that fits the results shown in Figure 1 to within 0.3% error (1 degree) is given by

$$T_s = k_1 x^3 + k_2 y^3 + k_3 x^2 y + k_4 xy^2 + k_5 x^2 + k_6 y^2 + k_7 xy + k_8 x + k_9 y + k_{10} \quad (1)$$

where $x = \log_{10}[f(CH_4)]$ and $y = \log_{10}[f(CO_2)]$. A one-bar atmosphere is assumed, so $f(CO_2) = pCO_2$ in atm. The coefficients k_i are listed in Table I. The numerical fits were performed over the range: 10^{-5} atm $< pCO_2 < 10^{-2}$ atm, $10^{-5} < f(CH_4) < 10^{-2}$.

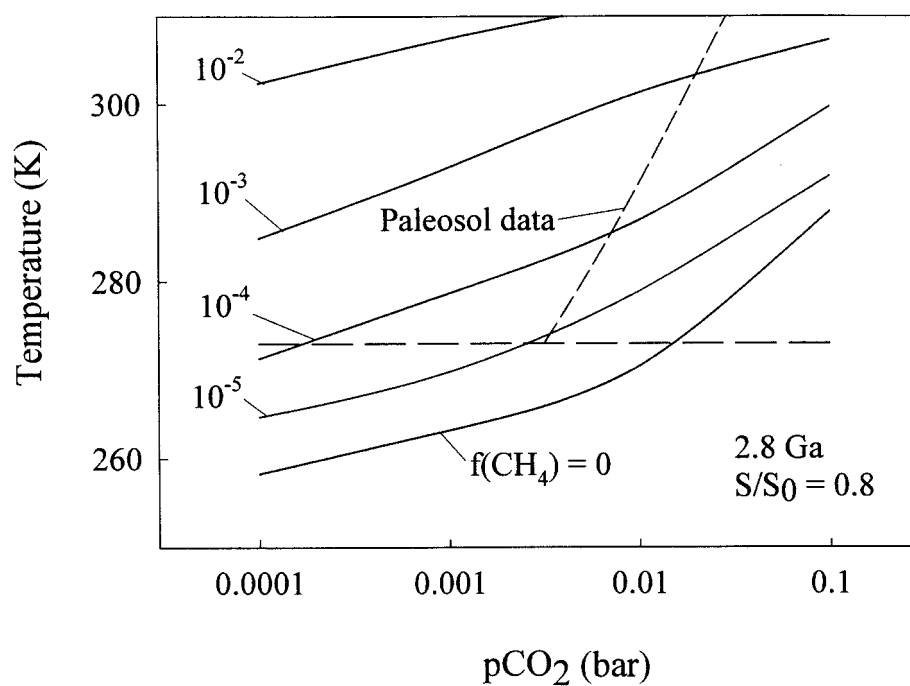*Figure 1.* Surface temperature as a function of *pCO₂* and *f*(CH₄). The short-dashed curve represents the upper limit on pCO_2 based on the absence of siderite in 2.8-billion-year-old paleosols (Rye *et al.*, 1995). The long-dashed line shows the freezing point of water. The assumed solar flux is 0.8 times the present value, so the calculations are appropriate for 2.8 Ga.

TABLE I

CH_4/CO_2 greenhouse fitting coefficients

k_1	–0.7542
k_2	0.2625
k_3	–0.9025
k_4	–0.4325
k_5	–9.1088
k_6	1.3738
k_7	–9.6900
k_8	–28.1973
k_9	–4.8311
k_{10}	301.0699

We next assume that methanogens were widely distributed in the late Archean biosphere and that they were producing methane primarily according to reaction R1. Reaction R1 can be rewritten as:

$$CO_2(g) + 4\,H_2(g) \rightarrow CH_4(g) + 2\,H_2O(\ell), \tag{R2}$$
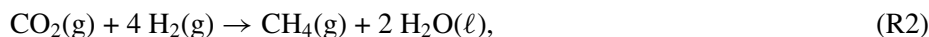
where 'g' or 'ℓ' denotes the gaseous or liquid phase, respectively. Thermodynamic data for the gaseous reactants and products can be used, even though these reactions occur in liquid solution, because by Henry's Law the dissolved species have the same free energy as the gases with which they are in equilibrium.

Following Kral *et al.* (1998), we assume that methanogenic bacteria will consume hydrogen and produce methane until the Gibbs free energy change for this reaction drops to less than 8.5 kcal (or 35.6 kJ) per mole, the energy required to synthesize ATP. Anaerobic, hydrogen-utilizing bacteria appear to be thermodynamically energy-limited (though not necessarily by this particular metabolic requirement) while aerobic chemosynthetic bacteria are not (Seitz *et al.*, 1990; Conrad, 1996). According to the Nernst Equation, the free energy change for reaction (R2) is given by

$$\Delta G = \Delta G_0 + RT \ln Q, \tag{2}$$

where

$$Q = \frac{pCH_4 \cdot aH_2O^2}{pCO_2 \cdot pH_2^4}.$$

The partial pressures are expressed in atm, and the activity of H_2O is assumed to be unity. ΔG_0 ($= -253.05 + 0.4098\,T$ kJ mol^{-1}) is the change in Gibbs free energy under standard conditions of temperature and pressure (*ibid.*) The actual reaction as performed by methanogens is not reversible; rather, it consists of separate oxidative and reductive steps (Thauer, 1998). We ignore that complication. Furthermore, the actual free energy change that may support minimal metabolism may be as low as 10–15 kJ mol^{-1} (Conrad, 1996, Figure 2). However, the assumptions made above produce reasonable agreement with experimentally observed limits on hydrogen uptake (Kral *et al.*, 1988). We assume that T in Equation (2) is equal to T_s, i.e., we ignore latitudinal changes in surface temperature on the early Earth.

We take T_s to be a free parameter, constrained by the lack of evidence for glaciation at that time to be at least 280 K and probably higher. Once T_s is specified, we now have two Equations, (1) and (2), for three unknowns: pCH_4, pH_2, and pCO_2. We need one more Equation to close the system. That Equation comes from balancing the atmospheric redox budget. For the prebiotic Earth, the redox budget would contain only abiotic terms. Let us see what they are first and then consider how they would be modified by biology. We can represent reducing power in terms of molecular hydrogen, H_2. To first order, the loss of H_2 to space must have been balanced by an equivalent input of reduced volcanic gases (Walker, 1977; Kasting

and Brown, 1998). Note that it is not just volcanic H_2 itself that matters. For example, outgassing of CO counts as a source of hydrogen because it is oxidized to CO_2

$$CO + H_2O \rightarrow CO_2 + H_2. \tag{R3}$$

This reaction is not direct but, rather, is catalyzed by the byproducts of water vapor photolysis. Similar reactions can be written for other reduced volcanic gases. Rainout of reduced and oxidized gases and incorporation of reduced compounds into sediments should also be considered in a complete model.

We balance volcanic outgassing with escape to space to get a first-order estimate of the atmospheric redox budget. According to Holland (1978, p. 291–292), the combined volcanic outgassing rates of H_2, CO, and SO_2 are 2.8×10^{12} mol yr^{-1}, equivalent to $\sim 1 \times 10^{10}$ H_2 molecules cm^{-2} s^{-1}. This is probably a lower limit on the outgassing flux in the late Archean because the geothermal heat flux was higher (Turcotte, 1980) and because the primitive mantle may have been more reduced at that time (Kasting *et al.*, 1993) [but see Canil (1997) for a different view]. If hydrogen was escaping at the diffusion-limited rate (Hunten, 1973; Walker, 1977), the escape rate would have been

$$\phi_{lim}(H_2) \cong 2.5 \times 10^{13} f_{tot}(H_2) cm^{-2} s^{-1}, \tag{3}$$

where

$$f_{tot}(H_2) = f(H_2) + 2f(CH_4) + f(H_2O) + \dots . \tag{4}$$

Here, $f_{tot}(H_2)$ is the total mixing ratio of hydrogen in the stratosphere in all of its chemical forms, weighted by the number of H_2 molecules they contain. (As noted above, we assume a total atmospheric pressure of 1 atm, in which case $f(H_2) = pH_2/1$ atm, and similarly for CH_4). For most of the atmospheres considered here, the stratosphere is quite dry, so $f(H_2O)$ can be neglected in Eeuation (4) compared to $f(H_2)$ and $f(CH_4)$.

To get some numbers out of this, set $\phi_{lim}(H_2)$ equal to the modern outgassing rate of reduced gases. Then, $f_{tot}(H_2) \cong 1 \times 10^{10}$ cm^{-2} s^{-1}/2.5×10^{13} cm^{-2} s^{-1} = 4×10^{-4}, or 400 ppm. The actual value of $f_{tot}(H_2)$ on the prebiotic Earth was probably higher than this because volcanic outgassing rates were higher and because hydrogen may have escaped at less than the diffusion-limited rate. (An O_2-poor, CO_2-rich upper atmosphere should have been cold, like that of Venus or Mars today, so that energy considerations may have reduced the escape rate below the diffusion limit). As a best guess, we will assume that at 2.8 Ga $f_{tot}(H_2)$ was 5 times higher than this, or 2×10^{-3}.

Finally, it is convenient to solve for the atmospheric methane mixing ratio by inverting Equation (4) (neglecting H_2O and other hydrogen-bearing species) to get

$$f(CH_4) \cong [f_{tot}(H_2) - f(H_2)]/2. \tag{5}$$

TABLE II

Equilibrium mixing ratios of CO_2, H_2, and CH_4

$T_s(K)$	$f(CO_2)$	$f(H_2)$	$f(CH_4)$
$f_{tot}(H_2) = 2 \times 10^{-4}$			
280	1.51(–3)	8.14(–6)	9.59(–5)
290	1.73(–2)	9.87(–6)	9.51(–5)
300	1.10(–1)	1.31(–5)	9.34(–5)
$f_{tot}(H_2) = 2 \times 10^{-3}$			
280	2.05(–5)	4.26(–5)	9.79(–4)
290	4.44(–4)	4.41(–5)	9.78(–4)
300	9.29(–3)	4.38(–5)	9.78(–4)
$f_{tot}(H_2) = 6 \times 10^{-3}$			
290	3.39(–5)	1.11(–4)	2.94(–3)
300	1.11(–3)	9.82(–5)	2.95(–3)

Equations (1), (2), and (5) comprise a system of three algebraic equations that can be solved using a standard, nonlinear equation solver such as Newton's method.

For the post-biotic Earth, the atmospheric redox balance is complicated by burial of organic material in sediments and by reaction of photosynthetically-produced O_2 with reduced materials such as ferrous iron. We argue below that burial of organic matter would not have reduced $f_{tot}(H_2)$ much below the levels predicted here because methanotrophs would have been inefficient at consuming atmospheric CH_4. The effect on the atmospheric redox budget is still hard to predict, however. If organic carbon burial dominates, then $f_{tot}(H_2)$ would be smaller than predicted here; if iron oxidation dominates, then $f_{tot}(H_2)$ could have been larger. In recognition of these uncertainties, we have performed calculations for $f_{tot}(H_2) = 2 \times 10^{-4}$ (10 times lower than our best guess) and 6×10^{-3} (3 times higher). As shown below, the magnitude of $f_{tot}(H_2)$ determines how important methane would have been in the atmospheric greenhouse.

3. Results

3.1. ANAEROBIC ECOSYSTEM ONLY

The system of Equations above was solved for surface temperatures of 280 K, 290 K, and 300 K, and for the three values of $f_{tot}(H_2)$ listed above. The results are given in Table II. The general conclusions are as follows:
1) The calculated ratio $f(CH_4)/f(H_2)$ is of the order of 10–30 for most of the cases studied. The higher ratios correspond to the more hydrogen-rich atmospheres.

The calculated CH_4/H_2 ratio becomes even higher if the critical value of ΔG in Equation (2) is assumed to be < 35.6 kJ mol^{-1}. Thus, if methanogen metabolism was limited by energy considerations, as assumed here, at least 90% of the atmospheric H_2 would have been converted to CH_4. This prediction is in agreement with the conclusions reached by Kral *et al.* (1998).

The calculated CH_4/H_2 ratio depends strongly on the amount of greenhouse warming provided by methane. An earlier version of this model that derived less greenhouse warming from methane (because of differences in absorption coefficients) predicted lower H_2 abundances, and hence higher CH_4/H_2 ratios, because it required higher CO_2 levels to maintain a given surface temperature. High CO_2 levels drive reaction (R1) to the right by decreasing the magnitude of the concentration-dependent term in Equation (2).

A caveat should be added here, however: methanogen productivity may have been limited by the availability of nutrients other than CO_2 and H_2. Phosphate and nitrate are limiting nutrients today in many terrestrial and marine ecosystems. Many methanogens can fix nitrogen (Eady, 1991), but phosphate would presumably have been in short supply in the Archean as it is today. A more detailed model of the Archean ecosystem would be needed to estimate how important nutrient limitation might have been.

2) Plausible scenarios exist in which atmospheric CH_4 is more abundant than CO_2. This happens for hydrogen-rich atmospheres but not for hydrogen-poor ones. Thus, if the Archean atmosphere was hydrogen-rich, much of the greenhouse warming needed to compensate for reduced solar luminosity may have been provided by biogenic methane. This observation, in turn, has two interesting corollaries:

  a) The oft-repeated suggestion (Walker *et al.*, 1983; Kasting *et al.*, 1983) that the rise of atmospheric O_2 may have triggered the Huronian glaciation at 2.3 Ga by lowering atmospheric CH_4 levels appears to be quantitatively viable. Note that, even though CH_4 would have been oxidized to CO_2, the resulting greenhouse effect would have been much smaller than before because CH_4 is a stronger greenhouse gas than CO_2 and because atmospheric CO_2 is in equilibrium with a much larger reservoir of dissolved CO_2 in the oceans. Hence, its atmospheric concentration would not have increased proportionately to the amount of CH_4 that was oxidized.

  b) A hydrocarbon smog layer may have existed during part or all of the Archean. Photochemical model calculations by Brown (1999) (see also Zahnle, 1986) indicate that hydrocarbon smog is produced in such atmospheres whenever $f(CH_4)/f(CO_2) > 0.6$. Thus, the prediction by Lovelock (1988) and by Sagan and Chyba (1997) that such a smog layer may have existed also appears to be justified. A hydrocarbon haze layer could have acted as a screen against solar ultraviolet radiation, and this in turn has implications for early biological evolution and for atmospheric photochemistry.

3.2. ADDING THE HIGH-PRODUCTIVITY, O_2-RICH REGIONS

The model described above is admittedly oversimplified. As mentioned earlier, organic biomarkers indicate the existence of both cyanobacteria and eukaryotes by 2.7 Ga. Morphologic evidence (Schopf, 1993) would place the origin of cyanobacteria even earlier, around 3.5 Ga. The isotopically light kerogens at 2.8 Ga are also most easily explained if O_2 was present in at least some environments. Hayes (1983, 1994) suggested that the kerogens were formed by a double fractionation process in which methanogens generated isotopically light CH_4, and then methanotrophs consumed this CH_4 and produced even lighter organic matter. Most modern methanotrophs use O_2 as the oxidant

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O, \tag{R4}$$

so the presence of free O_2 is suggested by this interpretation.

A physical model that can account for O_2-rich regions in an otherwise anoxic environment was outlined by Kasting (1992). Diffusion of gases between the atmosphere and ocean is limited by transport through a thin boundary layer at the ocean's surface. The transport rate can be characterized by a 'piston velocity', v_{pis}, which for O_2 is on the order of 4 m day^{-1}. Hence, if significant photosynthetic production of O_2 was occurring within the water column, concentrations of dissolved O_2 in the surface ocean could have been vastly out of equilibrium with the overlying atmosphere. For a primary productivity rate of 1 g C m^{-2} day^{-1} (Riley and Chester, 1971, p. 264), the O_2 production rate, P, is 0.083 mol m^{-2} day^{-1}, and the corresponding steady-state dissolved O_2 concentration (P v_{pis}) is 21 μM. At 15 °C, this would be in equilibrium with 0.016 atm of gaseous O_2, or 0.08 PAL (times the Present Atmospheric Level). This is well above the limit of 0.01 PAL O_2 required to support aerobic metabolism and eukaryotes (Chapman and Schopf, 1983). It represents an upper limit on dissolved O_2 in the Archean surface ocean because this calculation neglects loss of O_2 by reaction with reduced compounds (Fe^{++}, $S^=$, H_2) diffusing into the high-productivity regions.

Note that photosynthetic production of O_2, even at substantial rates, does *not* necessarily imply buildup of O_2 in the atmosphere. Photosynthesis can be written schematically as

$$CO_2 + H_2O \rightarrow CH_2O + O_2. \tag{R5}$$

Whether or not any net O_2 is produced depends on what happens to the organic carbon (CH_2O) that is generated. If the CH_2O is buried in sediments, then O_2 is left behind. If, on the other hand, it is degraded by fermentation followed by methanogenesis, then the overall decay reaction may be written as

$$2\,CH_2O \rightarrow CO_2 + CH_4. \tag{R6}$$

If all of the organic carbon were degraded in this way, it is easy to demonstrate that the amount of CH_4 produced would be exactly sufficient to titrate out the O_2 pro-

duced by reaction (R5). Thus, there is no inherent contradiction in contemplating CH_4-rich atmospheres coupled with substantial photosynthetic O_2 production.

If such 'oxygen oases' existed on the Archean Earth, they should have harbored methanotrophs. Methane that diffused into these regions from the atmosphere could have been profitably metabolized by aerobic methanotrophic bacteria. It is interesting to consider whether such bacteria would have drawn down atmospheric CH_4 concentrations below the levels discussed here (10^{-5} – 10^{-2} atm). Unfortunately, one cannot apply the same type of thermodynamic analysis as presented above because H_2-oxidizers (and, by implication, CH_4-oxidizers) do not approach the same free energy limitation that chemosynthetic anaerobes achieve; rather, their growth rate is limited by other processes (Seitz *et al.*, 1990; Conrad, 1996). However, we can still make a semi-quantitative assessment of their ability to metabolize atmospheric methane by comparing to kinetic data on CH_4 uptake by modern methanotrophs.

Growth rates for many organisms are observed to follow a Michaelis-Menton relationship which, for methanotrophs, has the form

$$V = V_{\max} \frac{f(CH_4)}{f(CH_4) + K_m}. \tag{6}$$

Here, $V_{\max}$ is the maximum growth rate and K_m represents the half-saturation value for methane concentration. Most methanotrophs that have been grown in pure cultures exhibit K_m values of $(4.6–381) \times 10^{-4}$, equivalent to 0.8–66 μM dissolved CH_4 (Conrad, 1996). (To maintain consistent notation, we continue to express gaseous CH_4 concentrations in terms of mixing ratio, remembering that for a one-bar atmosphere this is the same as partial pressure). Soil microorganisms are able to metabolize CH_4 at much lower levels. K_m values as low as 7–14 ppmv (10–20 nM dissolved CH_4) have been reported in the literature (Conrad, 1996; Dunfield *et al.*, 1999). These organisms evidently account for a substantial sink for atmospheric CH_4, even though its modern concentration is only $\sim$ 1.6 ppmv. Recently, Dunfield *et al.* (1999) reported a mixed culture of methanotrophic bacteria that exhibits an apparent K_m value of 40–132 ppmv, or 56–186 nM dissolved CH_4. These bacteria were grown in chambers enriched to < 275 ppmv CH_4. When exposed to higher mixing ratios of CH_4 (1000 ppmv), however, the apparent K_m increased to values typical of pure cultures.

Applying this information to the Archean ecosystem is not straightforward. However, we can make two possibly useful observations. First, from an energetic standpoint, methane oxidation would have been less profitable during the Archean because O_2 levels were lower. Even in high-productivity regions of the surface ocean, equivalent O_2 concentrations would have been $\leq$ 0.08 PAL. If one applies the Nernst Equation to reaction (R4), the concentration-dependent term has the form

$$Q = \frac{pCO_2 \cdot aH_2O^2}{pCH_4 \cdot pO_2^2}. \tag{7}$$

Thus, to derive an equivalent amount of energy from this reaction as can be obtained by methanotrophs today, pCH_4 would have to have been higher by a factor of $1/(0.08)^2 = 156$. If energy was a consideration, even the lowest reported K_m values for methane-consuming bacteria in soils would thus be scaled up to over 1000 ppmv, or $f(CH_4) = 10^{-3}$. This suggests that methanotrophs would not have been able to pull atmospheric CH_4 down below the values considered here. Alternatively, one can argue that Archean methanotrophs, being exposed to relatively high concentrations of atmospheric CH_4, would have exhibited K_m values close to those seen in pure modern cultures. This argument also suggests that Archean methanotrophs would have been unable to keep atmospheric CH_4 at low levels. Phylogenetic analysis might show whether high-K_m methanotrophs preceded low-K_m methanotrophs, as might be expected from these environmental considerations.

4. Discussion

Although the results of this modeling exercise are not as definitive as one might wish because of the inherent difficulty in specifying all of the relevant parameters, a plausible scenario for Archean environmental/biospheric evolution does emerge. Once methanogenic bacteria had become widespread on Earth, probably during the early Archean, methane became an abundant constituent of the atmosphere and an important contributor to the greenhouse effect. The atmospheric CO_2 partial pressure may have fallen from a few tenths of a bar or more (Kasting, 1993) to values not much higher than those at present. The decrease in CO_2 would have been driven by increased rates of silicate weathering on the continents brought about by CH_4-induced climatic warming. Continued growth of the continents during this time (Taylor and McLennan, 1995) would have accelerated the decline in atmospheric CO_2 by providing increased land area available for weathering. Uncertainties in the rate of continental growth, among other factors, make it difficult to predict just how fast or how far CO_2 levels would have declined.

   Atmospheric methane levels could not have risen too high, however, without other factors coming into play. As long as CH_4 remained less abundant than CO_2, methane would have helped to keep the early climate warm, and methanogens would have flourished. Once $f(CH_4)$ approached $f(CO_2)$, however, hydrocarbon smog would have started to form, and the surface would have been cooled by an 'antigreenhouse effect' (McKay et al., 1991). (In an antigreenhouse situation, as occurs today on Saturn's moon Titan, solar radiation is absorbed in the stratosphere, and energy is re-radiated back to space from that level, thereby reducing the amount of energy available to warm the planet's surface.) Antigreenhouse cooling would have slowed the growth of the methanogens, thereby reducing the supply of biogenic CH_4. This, in turn, would have reduced the amount of hydrocarbon smog formed and allowed the surface to warm back up. Based on the lack of evidence

for glaciation at this time, the climate system evidently stabilized at a mean surface temperature somewhat higher than today's value.

This negative feedback loop between atmospheric CH_4 levels and climate is similar to the negative feedback between atmospheric CO_2 and climate described by Walker *et al.* (1981), but it would have operated on a much shorter time scale. It also involves the biota directly, and in this sense is really 'Gaian' (Lovelock, 1988). In a very real sense, Earth's methanogenic Archean biota may have maintained a climate suitable for their existence.

Our ecosystem model is still oversimplified, of course. Bacteria performing anoxic photosynthesis are likely to have been present as well. Some of these, such as the green, non-sulphur photosynthetic bacteria, used hydrogen as the electron donor to reduce CO_2 and may have competed with the methanogens for atmospheric H_2.

Starting around 2.5 Ga, an increase in the spread of sulfur isotope ratios in sulfide and sulfate sediments suggests that sulfate began to become more abundant in the Archean oceans (Cameron, 1982; Canfield, 1998; Canfield *et al.*, 2000). At this point, sulfate reducing bacteria should have increased in abundance. Sulfate reducers have K_m values for H_2 consumption that are typically less than half those of methanogens (Zinder, 1993, p. 154), so methane production should have dropped off once they began to proliferate. Perhaps this is why the lightest kerogens are confined to the time right around 2.8 Ga. Indeed, the spread of sulfate reducers could, in principle, have triggered a steep decline in atmospheric CH_4 and, hence, triggered the Huronian glaciation. The timing seems a bit off, though, as the glaciation appears to have occurred somewhat later, between 2.45 and 2.22 Ga (Evans *et al.*, 1997). Furthermore, in the Huronian sequence itself (in southern Canada), the glacial deposits are underlain by sedimentary rocks that contain detrital uraninite and pyrite and are overlain by redbeds (Roscoe, 1969, 1973; Walker *et al.*, 1983). This is most easily explained if the glaciation was directly triggered by the rise of atmospheric O_2.

Two final points deserve mention. First, although the story presented here is reasonably self-consistent, it does *not* explain why atmospheric O_2 concentrations rose when they did. In particular, it remains a mystery why the rise of O_2 seems to have post-dated the appearance of cyanobacteria by at least 400 million years, and possibly much longer. A more reduced Archean mantle might explain this time lag because the volcanic O_2 sink would then have been larger (Kasting *et al.*, 1993), but this hypothesis appears to be at odds with the geologic evidence (Canil, 1997; Delano, in press). It seems more likely that, for one reason or another, cyanobacteria remained a minor part of the global ecosystem until $\sim$ 2.3 Ga. Alternatively, cyanobacteria were abundant but they subsisted mainly by anoxic photosynthesis prior to that time because H_2 and/or H_2S were readily available as electron donors.

A second unanswered question concerns the carbon isotope record. Apart from relatively brief positive excursions in the early and late Proterozoic (Knoll *et al.*, 1986; Karhu and Holland, 1996), the $\delta^{13}C$ values of marine carbonates have re-

mained more or less constant at $\sim$0‰ (Schidlowski *et al.*, 1983). If the isotopic fractionation between carbonates and organic carbon has remained approximately constant (which appears to be nearly true except near 2.8 Ga), the fraction of outgassed CO_2 buried as organic carbon has remained close to 20% throughout geologic time. As discussed by Holland (1978), this suggests that Earth's surface environment has always been operating as a closed system: the amount of reduced volcanic gases (primarily H_2 and CO) has always been just enough to bury 20% of the outgassed carbon in reduced form. But this, in turn, implies that hydrogen escape to space has always been negligible compared to burial of organic carbon. This is certainly true today. The modern H escape rate is about 100 times too slow to significantly affect the global redox budget. But it would not have been true for the high-CH_4 atmospheres considered here if hydrogen was escaping at the diffusion-limited rate. As mentioned earlier, H_2 may have been escaping more slowly in the past because of a cold upper atmosphere. This suggestion remains to be tested quantitatively. For now, we simply point out that the carbon isotope record provides an additional way of testing paleo-atmospheric models.

5. Conclusions

We have presented a simple, coupled ecosystem-climate model for the Archean environment. The model predicts that CH_4 was an important greenhouse gas at that time and that the surface temperature was stabilized by a feedback loop involving photochemical smog production and the growth rate of methanogens. Methanotrophs would also have existed in oxidizing regions of the surface ocean, but they are unlikely to have drawn atmospheric CH_4 down to low levels. The rise of atmospheric O_2 in the early Proterozoic would have signalled the end of this stage of Earth history and the beginning of the modern, CO_2/H_2O-dominated climate system.

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