Implications of present-day abiogenic methane fluxes for the early Archean atmosphere

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[1] During Earth's early history, greenhouse warming by atmospheric methane helped to maintain elevated surface temperatures. Here, we estimate the present-day abiogenic CH_4 flux generated by mineral alteration (serpentinization) at mid-ocean ridges, volcanic emissions, and geothermal sources; in addition, we assess the impact that abiogenic methane may have had on greenhouse warming during the early prebiotic Archean. Based on estimates of the rate of seafloor spreading and the degree of serpentinization within the oceanic crust, the flux of methane generated by serpentinized lithosphere is calculated to be $\sim$1.35 Mt CH_4 y^{-1}, while volcanic and geothermal sources are estimated to contribute $\sim$0.1 and $\sim$0.9 Mt CH_4 y^{-1}, respectively. Furthermore, it is shown that if atmospheric CO_2 partial pressures were above 0.01 bar, the present-day level of abiogenic methane production could have been sufficient to maintain above-freezing surface temperatures during the Archean. The very high temperatures ($\sim$70°C) that have been suggested for the early Archean, however, would have required extremely high methane fluxes or, more likely, greatly elevated atmospheric CO_2 levels. **Citation:** Emmanuel, S., and J. J. Ague (2007), Implications of present-day abiogenic methane fluxes for the early Archean atmosphere, *Geophys. Res. Lett.*, *34*, L15810, doi:10.1029/2007GL030532.
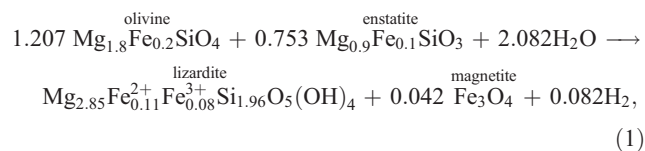
1. Introduction

[2] Methane is a greenhouse gas that plays a crucial role in Earth's climate system. Large anthropogenic emissions of CH_4 contribute to present-day global warming [*Intergovernmental Panel on Climate Change*, 2001], and high atmospheric CH_4 concentrations may have helped to maintain the warm surface temperatures that prevailed throughout much of Earth's early history [*Kiehl and Dickinson*, 1987; *Pavlov et al.*, 2000]. While present-day fluxes are dominated by anthropogenic and biogenic sources [*Etiope and Klusman*, 2002], it is unclear whether atmospheric methane levels during the early Archean ($\sim$3.8 Ga) were controlled by abiotic geological processes or methanogenic bacterial activity. The flux emitted by present-day natural biogenic sources ($\sim$170 Mt y^{-1}) [*Etiope and Klusman*, 2002; *Kvenvolden and Rogers*, 2005] is capable of sustaining relatively high atmospheric concentrations in a reducing early atmosphere, which may have resulted in a significant greenhouse effect [*Pavlov et al.*, 2000]; however, present-day abiogenic methane fluxes are orders of magnitude lower than biogenic sources, and their potential impact is uncertain.

[3] In addition to assessing the influence of CH_4 on global climate, establishing the level of abiogenic methane in the atmospheres of Earth-like planets is critical if CH_4 is to be used as an indicator for extraterrestrial life during missions such as NASA's proposed Terrestrial Planet Finder (TPF) program. Furthermore, abiogenic CH_4 represents a potential reactant in the synthesis of HCN polymers which may have served as crucial precursors for life on primitive Earth [e.g., *Matthews*, 1995].

[4] Although some studies have included methane fluxes related to hydrocarbon reservoirs in estimates of abiogenic production, here we exclude CH_4 that is produced from the breakdown of organic matter of biogenic origin, as well as methane formed directly by biological activity. Such a definition is necessary to assess the impact of methane production on the Archean atmosphere prior to the establishment of biological methanogenic pathways. In present-day Earth, there are three main sources of abiotic methane: water-rock interactions at mid-ocean ridges (0.1–9 Mt y^{-1}) [*Welhan and Craig*, 1979; *Sorokhtin et al.*, 2001; *Kasting and Catling*, 2003]; volcanic activity (0.34–6.2 Mt y^{-1}) [*Cadle*, 1980; *Kvenvolden and Rogers*, 2005]; and geothermal systems (0.9–6.3 Mt y^{-1}) [*Lacroix*, 1993; *Etiope and Klusman*, 2002]. In this paper we use recent, well-constrained geophysical data to reassess the CH_4 fluxes associated with serpentinization at mid-ocean ridges, volcanism, and geothermal sources, and we discuss the implications of abiogenic methane production for the early Earth.

2. Water-Rock Interaction at Mid-Ocean Ridges

[5] Serpentinization is a common reaction in the crust, hydrating olivine and pyroxene minerals to form serpentine and other products. Crucially for the generation of methane, during serpentinization some of the Fe^{2+} in the primary minerals is excluded from the silicate phase to form $Fe(OH)_2$ and magnetite [*Evans*, 2004], a process which liberates hydrogen. A balanced reaction for metaharzburgite, similar to that suggested by *Evans* [2004], can be written as

$$1.207 \underset{\text{olivine}}{Mg_{1.8}Fe_{0.2}SiO_4} + 0.753 \underset{\text{enstatite}}{Mg_{0.9}Fe_{0.1}SiO_3} + 2.082 H_2O \longrightarrow$$
$$\underset{\text{lizardite}}{Mg_{2.85}Fe^{2+}_{0.11}Fe^{3+}_{0.08}Si_{1.96}O_5(OH)_4} + 0.042 \underset{\text{magnetite}}{Fe_3O_4} + 0.082 H_2, \tag{1}$$

with methane being produced by Fischer-Tropsch synthesis [*Berndt et al.*, 1996],

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O. \tag{2}$$
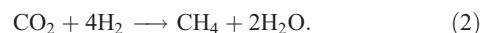
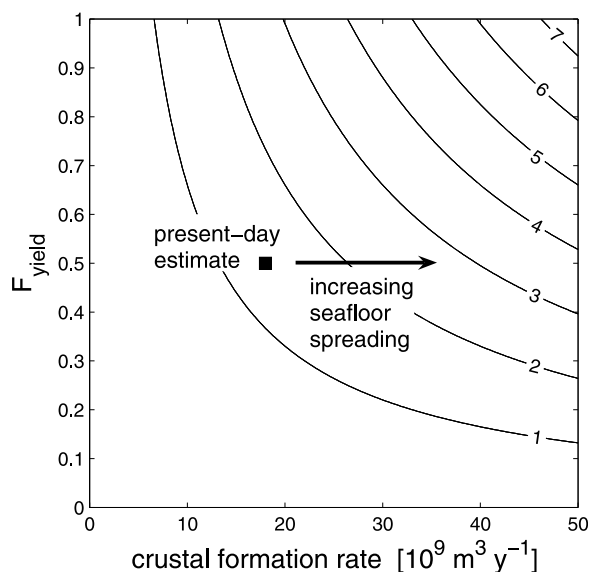[1]Department of Geology and Geophysics, Yale University, New Haven, Connecticut, USA.

Figure 1. Methane flux from serpentinization as a function of the formation rate of oceanic crust (R_{crust}) and methane yield (F_{yield}). Values marked on contour lines are in units of Mt y^{-1}.

Thus, the formation of 1 mole of serpentine potentially liberates ~0.021 moles of methane, and this ratio, together with an estimate for the global rate at which serpentinization occurs at mid-ocean ridges, can be used to obtain the overall contribution to the geological methane budget.

[6] Serpentinization typically takes place in young oceanic crust where hydrothermal activity is vigorous. However, while serpentine is a common mineral phase, it is far from being dominant in the oceanic lithosphere; seismic studies suggest that typical crust consists of up to 5% serpentinite by volume [*Carlson*, 2001], which, assuming a mineral density of 2550 kg m^{-3}, yields a mean crustal concentration of 451 mol lizardite m^{-3}. Thus, 1 cubic meter of crust could form 9.47 moles of CH_4. From a typical oceanic crustal depth of 6 km [*Sinha and Evans*, 2004] and a production rate of 3 km^2 y^{-1} [*Parsons*, 1982] a crustal formation rate, R_{crust}, of 1.8×10^{10} m^3 y^{-1} is obtained, which could generate 1.7×10^{11} moles or 2.7 Mt of methane annually. Importantly, H_2/CH_4 ratios in vents suggest that not all H_2 is converted into methane, so this value represents a maximum flux. However, an estimate for the methane yield ($F_{yield} = [CH_4]/([CH_4] + 1/4[H_2])$) can be obtained from a compilation of reported data [*Von Damm*, 1995; *Kelley et al.*, 2001], and such an analysis gives a mean value of 0.6 ± 0.09 based on 13 sets of measurements taken at different sites (1σ standard error). As this value may have been increased by microbial processes within the hydrothermal system, we conservatively set $F_{yield} = 0.5$, which produces an annual global flux of 1.35 Mt CH_4 y^{-1}. Notably, the method employed here, which is based firmly on empirical geophysical data, yields a value that is significantly smaller than that given by *Sorokhtin et al.* [2001] (9 Mt y^{-1}), and far higher than the commonly cited estimate of 0.1 Mt y^{-1} [*Welhan and Craig*, 1979]. Interestingly, our estimate is very similar to that calculated by *Kasting and Catling* [2003] (1.6 Mt y^{-1}) who used a different technique based on the heat-flux at mid-ocean ridges and the methane

concentration in fluids from peridotite-hosted hydrothermal systems; their method of calculation, however, was particularly sensitive to CH_4 concentrations and the flux estimate was recently increased by a factor of ~10 [*Kharecha et al.*, 2005]. In light of our calculated value, such a high figure is likely to be an overestimate due to the elevation of CH_4 levels by methanogenic bacteria in vent systems [*Brazelton et al.*, 2006].

[7] While all of the values used in this calculation are subject to some degree of uncertainty, the methane yield and crustal formation rate are perhaps the least constrained during geological time, and the effect of these two parameters is summarized in Figure 1. Crucially, the rate of seafloor spreading may have varied significantly throughout Earth's history, and could have been as much as 70% faster than the present rate for parts of the Phanerozoic [*Berner*, 1990]. Because oceanic crustal depth typically increases with increasing spreading rate [*Sinha and Evans*, 2004], R_{crust}, and subsequently the rate of methane generation, may have been much higher in the past. Although R_{crust} is likely to have varied over geological time, it is unclear if changes in seafloor spreading will have influenced F_{yield}; potentially shorter residence times in vigorously convecting hydrothermal systems could lead to lower methane yields, although relatively little is known about the kinetics of methane formation in the crust [*Berndt et al.*, 1996; *Horita and Berndt*, 1999]. In our calculations, we have also assumed that all the methane introduced into the oceans eventually reaches the atmosphere. Although some methane is oxidized in present-day oceans [*Ward et al.*, 1987], in the presumably anoxic conditions of the early Archean, even less methane is expected to be lost to oxidation.

3. Methane Associated With Volcanism

[8] Gases emitted from fumaroles often have significant CH_4 concentrations [e.g., *Giggenbach and Matsuo*, 1991], and global estimates of "volcanic" CH_4 vary widely from 0.34 to 6.23 Mt y^{-1} [*Cadle*, 1980; *Lacroix*, 1993]. These estimates, however, do not distinguish between mantle-derived methane and CH_4 produced by water-rock interactions in hydrothermal systems associated with volcanic activity, both of which may be present in fumarole gases. As methane production during water-rock interactions is dealt with separately in this study, the term volcanic is used to indicate methane of mantle origin only.

[9] The most straightforward approach to calculating volcanic CH_4 involves estimating the mantle degassing rate of CO_2 which is then multiplied by a representative value for the volcanic CH_4/CO_2 ratio. Such a method was used by *Lacroix* [1993], yielding a global flux of 0.78−6.23 Mt y^{-1}. While the representative ratio (2.6×10^{-3}) was based on a study which examined gases in different fumaroles, hydrothermal generation of methane is likely to have been the dominant source in those with elevated concentrations [*Giggenbach and Matsuo*, 1991]. A recent study at Mauna Loa, Hawaii, suggests that mantle-derived CH_4/CO_2 ratios are likely to be at most 3.1×10^{-4} [*Ryan et al.*, 2006]; even lower ratios have been observed in some volcanic systems [*Holland*, 1984; *Giggenbach and Matsuo*, 1991]. Adopting the value from Mauna Loa and a global volcanic CO_2 flux of 300 Mt y^{-1} [*Morner and Etiope*, 2002] yields a value of
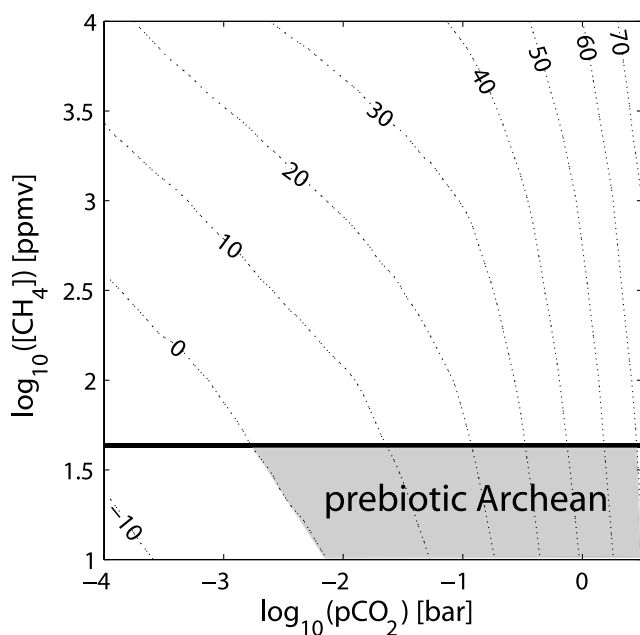
Figure 2. Mean surface temperature as a function of CO_2 partial pressure and atmospheric methane concentrations. Contour lines indicate approximate temperatures in °C. The solid black line shows the atmospheric concentration of methane in a reducing atmosphere corresponding to the maximum estimate for the present-day abiogenic methane flux. The shaded area represents the range of conditions likely to have prevailed during the early prebiotic Archean; temperatures have a lower bound of 0°C and an upper limit of 70°C. Contours are based on data from *Kasting and Howard* [2006].

0.093 Mt CH_4 y^{-1}, an estimate which includes volcanic methane emitted at mid-ocean ridges. While ocean island magmatism is not typical of most volcanism on Earth, the value based on data from Mauna Loa is likely to more closely represent the mantle-derived methane flux than previous estimates.

4. Abiogenic Geothermal Methane

[10] Significant levels of methane production are often associated with continental geothermal regions, with global estimates in the range 0.9–6.3 Mt y^{-1} [*Lacroix*, 1993; *Etiope and Klusman*, 2002]. However, the sources of methane typically included in this category are diverse and include two biogenic and two abiogenic sources [*Welhan*, 1988]: (1) thermal breakdown of organic matter at elevated temperatures; (2) bacterial production within the crust; (3) mantle outgassing of methane; and (4) abiogenic synthesis at high temperature (>300–400°C). In an attempt to assess the relative importance of each of these processes, *Welhan* [1988] reviewed the isotopic compositions of methane from different geological settings and concluded that most geothermal methane forms during the thermocatalysis of organic matter, although some is also produced via abiogenic synthesis. Thus, a large proportion of geothermal methane is likely to be of biogenic origin, with abiogenic geothermal methane representing only a small fraction of

the estimates reported above; quantifying this fraction, however, has not yet been achieved, and we assume abiogenic geothermal methane to be represented by the lower end of previous estimates (0.9 Mt y^{-1}).

5. Implications for the Early Earth

[11] Based on the values presented here for the contribution of the various abiogenic processes (serpentinization, volcanoes, and geothermal regions), the total present-day abiogenic methane flux is estimated to be of the order of 2.3 Mt y^{-1}, at the lower end of previous estimates (1.3–21.4 Mt y^{-1}). In the reducing atmosphere of the early Archean, the present day flux would have produced a methane concentration of ~4 ppmv [*Pavlov et al.*, 2000].

[12] The two main controls on surface temperature are usually considered to be CO_2 and CH_4 concentrations, and the effect of these two parameters is summarized in Figure 2. While the contours are approximate and will change as new atmospheric models are developed, the temperature effects of methane (including its photochemical products) are likely to be similar to those depicted in Figure 2, particularly for CH_4/CO_2 ratios smaller than ~0.1 (J. Kasting, personal communication, 2007).

[13] Two crucial observations provide constraints for the environmental conditions during the Archean: (1) sediments, such as the Banded Iron Formations, were formed in liquid water, so mean surface temperatures must have been above freezing; (2) isotopic data from sediments formed between 3.3–3.5 Ga indicates that temperatures may have been as high as 70 ± 15°C [*Knauth and Lowe*, 2003]. Assuming abiogenic methane fluxes within the range of present-day estimates, a minimum value for pCO_2 of 10^{-3}–10^{-2} bar is required for temperatures to have remained above freezing (see Figure 2, shaded region). To reach temperatures above 55°C, however, would have required CO_2 partial pressures several orders of magnitude higher than those apparently recorded in 2.75 Ga paleosols (<10^{-2} bar) [*Rye et al.*, 1995].

[14] In addition to high CO_2 levels, elevated surface temperatures can also be achieved by increasing CH_4 concentrations. More vigorous mantle convection during the early Archean may have resulted in higher rates of mantle outgassing and mid-ocean ridge serpentinization [*Pavlov et al.*, 2000], while comet impacts may have also contributed to elevated atmospheric CH_4 levels during the early Archean; estimates suggest that impacts could have produced more than 500 Mt y^{-1} before 3.5 Ga [*Kress and McKay*, 2004], although *Kasting* [2005] has calculated a much lower figure of 4 Mt y^{-1}. However, even with these additional sources, which may have produced atmospheric methane concentrations in the range 10^3–10^4 ppmv [*Pavlov et al.*, 2000], CO_2 levels of 0.1–1 bar are still necessary to have warmed the surface to 55°C, a conclusion which is consistent with *Kasting and Howard* [2006].

[15] Evidence that high levels of atmospheric CO_2 did indeed prevail during the early Archean can be found in the geological record: the presence of nahcolite (NaHCO$_3$) and an "aggressive" weathering regime in some sediments from 3.3–3.5 Ga are most easily explained by elevated CO_2 levels [*Lowe and Tice*, 2004]. Siderite beds in some Archean sedimentary formations have also been interpreted

as evidence for high CO_2 concentrations [*Ohmoto et al.*, 2004], although this is inconsistent with the absence of siderite in Archean paleosols [*Rye et al.*, 1995]. High CO_2 concentrations may have been maintained by more efficient tectonic recycling of CO_2 or by reduced transfer of CO_2 to the oceanic crust [*Lowe and Tice*, 2004]; the latter mechanism could have reflected a lower amount of continental crust available for weathering [*Young*, 1991; *Lowe*, 1994]. However, such interpretations of the history of Earth's early atmosphere have been challenged in some studies [*Kasting and Howard*, 2006; *Sleep and Hessler*, 2006; *Kasting et al.*, 2006], and whether or not high surface temperatures were widespread during the early Archean remains unresolved.

6. Concluding Remarks

[16] In this paper we assess the fluxes of abiogenic methane and estimate the combined production rate of serpentinization at mid-ocean ridges, volcanic outgassing, and geothermal sources to be ~2.3 Mt CH_4 y^{-1}. While the value is relatively small, representing approximately 0.4% of the total present-day methane budget, abiogenic CH_4 could have been an important greenhouse gas during Earth's early development prior to the rise of methanogenic bacteria. However, to maintain mean surface temperatures in excess of 55°C, atmospheric pCO_2 would have needed to have been much higher than 0.1 bar. To further constrain the atmospheric conditions during the early part of Earth's history, more data concerning surface temperatures are required.

[17] Fundamental questions still remain regarding the role played by CO_2 and CH_4 during the Archean. If CO_2 levels and surface temperatures were indeed high during the early part of the Archean, the effect of falling pCO_2 on the evolving biota is unclear, although it is tempting to suggest that more temperate and less acidic surface conditions could have facilitated the proliferation of methanogens and other forms of bacteria. Once biological methanogenesis was well established, biogenic CH_4 production may have stabilized and regulated surface temperatures, effectively maintaining conditions that were presumably favorable to early life on the surface of Earth.

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