

Methane in the early atmosphere of the Earth

J. F. Kasting

Department of Geosciences, The Pennsylvania State University,
University Park, PA 16802, USA

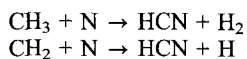
The currently prevailing view of Earth's prebiotic atmosphere is that it was a weakly reducing mixture of CO₂ and N₂, with smaller amounts of H₂, CO, and reduced sulphur gases (Walker *et al.*, 1983; Kasting, 1993). Highly reduced gases such as CH₄ and NH₃ are generally considered to have been present only in low concentrations because their sources would have been small and because they would have been destroyed by photolysis and by reactions with OH and O radicals produced from photolysis of H₂O and CO₂.

Abiotic sources of methane

If the early mantle were more reduced, however, as suggested by Kasting *et al.* (1993), volcanic gases released at depth from midocean ridge hydrothermal vents could have contained appreciable concentrations of CH₄ (Kasting and Brown, in press). Indeed, if the oxygen fugacity of the upper mantle were more than one log unit below the present value (which is near the QFM mineral buffer), most of the carbon released from the mid-ocean ridge vents should have been in the form of CH₄ instead of CO₂, as it is today. At current outgassing rates, the CH₄ flux would have been on the order of $(1-2) \times 10^{12}$ mol/yr (Marty and Jambon, 1987). Photochemical model calculations (Kasting and Brown, in press) indicate that this would have produced an atmospheric CH₄ concentration of 50–100 ppmv.

Effects of methane on organic synthesis and climate

The presence of this much CH₄ in the prebiotic atmosphere could have had important implications for the origin of life because it would have permitted formation of HCN by the mechanism suggested by Zahnle (1986). In this mechanism, N atoms produced by dissociative recombination of N₂⁺ in the ionosphere flow downwards and react with CH₃ and CH₂ radicals produced by methane photolysis in the stratosphere:

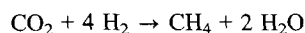


CH₄ concentrations of 100 ppmv or more would

also have been enough to affect the early climate. Preliminary calculations by using a radiative-convective climate model indicate that 100 ppmv of CH₄ would have provided an additional 14 W/m² of radiative forcing at the tropopause. This is approximately equivalent to the effect of 4 CO₂ doublings. Thus, atmospheric CO₂ levels could have been ~16 times lower than they would otherwise need to have been to compensate for the faint young Sun (Kasting, 1993). Additional calculations on the radiative effect of CH₄ which include the effect of absorption of solar radiation in the near-IR region are being carried out at the present time and will be reported at the meeting.

Archaean methane levels

Once life had arisen on Earth, the atmospheric CH₄ abundance should have risen because biological sources of CH₄ would have been available. Methanogenic bacteria produce CH₄ by reactions such as



The present biological source of CH₄ is approximately 3×10^{13} mol/yr. If the Archaean atmosphere were still anoxic, as many investigators believe (Walker *et al.*, 1983; Kasting, 1993), a CH₄ flux of this magnitude could have produced an atmospheric CH₄ mixing ratio as high as 3×10^{-3} , or 3000 ppm, at that time (Kasting and Brown, in press). Such a CH₄ abundance would have had a major warming effect on climate. Calculations are underway to determine exactly how much warming could have resulted. Rye *et al.* (1995) have placed upper limits on atmospheric CO₂ during the Archaean based on palaeosols. Their estimate is at least 20 times lower than the amount needed to compensate for the reduced solar luminosity at that time. Greenhouse warming by CH₄ may resolve the question of why the Archaean oceans were not completely frozen.

Changes in mantle redox state and the rise of atmospheric O₂

CH₄ would only have been abundant in the Archaean atmosphere if the atmosphere was still anoxic at that

time. Whether or not this was the case is still vigorously debated by different investigators. The relative constancy of the ^{13}C content of carbonate minerals back through time implies that the rate of organic carbon burial, and hence of O_2 production, has remained constant for at least the last 3.5 billion years. Some investigators would argue that this implies that atmospheric O_2 levels were also appreciable throughout the geologic record.

This argument, however, presupposes that the available O_2 sinks were also constant with time. In reality, volcanic gases could have consumed all of the O_2 produced by photosynthesis during the first half of Earth's history. Increased volcanic outgassing rates alone could not explain this because the rate of organic carbon burial should scale with the volcanic outgassing rate (because the carbon isotopes imply that a constant fraction of outgassed CO_2 was buried as organic carbon). However, if the early mantle was more reduced, as suggested above, then volcanic gases released during the early part of Earth's history may have been much more reducing than today. They would have become more oxidized with time as the mantle was progressively oxidized by subduction of

water followed by outgassing and escape of hydrogen. Atmospheric O_2 finally rose to appreciable levels around 2.2–2.0 Ga when the release rate of reduced gases fell below the rate of organic carbon burial.

References

- Kasting, J.F. (1993) *Science* **259**, 920–6.
- Kasting, J.F. and Brown, L.L. In: *The Molecular Origins of Life: Assembling the Pieces of the Puzzle*, ed. Brack, A. (Cambridge Univ. Press, New York, in press).
- Marty, B. and Jambon, A. (1987) *Earth Planet. Sci. Lett.*, **83**, 16–26.
- Rye, R., Kuo, P.H. and Holland, H.D. (1995) *Nature*, **378**, 603–5.
- Walker, J.C.G., Klein, C., Schidlowski, M., Schopf, J.W., Stevenson, D.J. and Walter, M.R. (1983) In: *Earth's Earliest Biosphere: Its Origin and Evolution* (ed. Schopf, J. W.) 260–90 (Princeton University Press, Princeton, New Jersey).
- Zahnle, K.J. (1986) *J. Geophys. Res.*, **91**, 2819–34.