Methane and climate during the Precambrian Era

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Geological and biological evidence suggests that the Earth was warm during most of its early history, despite the fainter young Sun. Paleosol data¹ have been used to estimate upper bounds on atmospheric CO₂ in the Late Archean/Paleoproterozoic (2.2-2.8 Ga), suggesting 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. The greenhouse effect of methane, though, is smaller than previously estimated and is opposed by cooling induced by organic haze. Hence, the CO₂ partial pressure required to offset 20% reduced solar luminosity at 2.8 Ga is of the order of 0.03 bar, or ~100 times the present atmospheric level (Fig. 1). This is higher than the published paleosol curve of Rye et al., but remains consistent with their analysis. Warming by ethane, C₂H₆, is also important in the new model.

Other parts of the methane story remain largely unchanged by this result. The rise of O_2 at 2.45 Ga should have caused a decrease in CH₄ which may have triggered the Paleoproterozoic glaciations. CH₄ concentrations may have recovered after that time and may be at least partly responsible for the ice-free climate of the mid-Proterozoic. A second rise in O_2 , and accompanying decrease in CH₄, could have triggered the Snowball Earth ice ages of the Neoproterozoic. This whole sequence of events, including the changes in O_2 , could plausibly have been driven by a gradually decreasing flux of hydrogen from reactions of water with ultramafic crust.



Figure 1 Mean surface temperature at 2.8 Ga as a function of atmospheric CO_2 and CH_4 . (From ref. 2)

Rye, Holland, and Kuo (1995) *Nature* **378**, 603-605.
Haqq-Misra *et al.* (2008) *Astrobiol.* **8**, 1127-1137.

What do pore fluid profiles of sulfate indicate about methane fluxes and amount of gas hydrates?

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Methane flux to the gas hydrate (GH) stability zone is an important factor that controls GH concentration. To assess the CH₄ fluxes and relate them to GH concentration, pore fluid data were obtained from pressurized and non-pressurized cores, in two passive margin basins offshore India, from a convergent margin site in the Andaman Sea, and from several sites on the convergent Cascadia margin. GHs are present at all these sites, though their abundance varies from site to site. δ^{13} C of dissolved inorganic carbon (DIC) is key to inferring carbon sources, metabolic paths of organic matter (OM) diagenesis, and CH₄ fluxes in these anoxic marine sediments.

The sulfate-methane transition (SMT) zone is the upper boundary for marine GH occurrence. In this redox transition zone, a microbial consortium mediates anaerobic oxidation of methane (AOM) coupled with SO_4^{2-} reduction. This reaction produces one mole of HCO_3^- per one mole of SO_4^{2-} reduced. Sulfate reduction coupled with anaerobic OM oxidation, however, produces approximately 2 moles of HCO3⁻ per mole SO_4^{2-} reduced. The observation that the slope and linearity of SO_4^2 concentration profiles can be directly related to the CH₄ flux at the SMT is applicable only if AOM is the dominant reaction responsible for the dissolved SO_4^{2-} profiles. At all the sites mentioned above, as at most other published sites, the data suggest that both SO₄²⁻ reducing pathways are active and their relative importance varies from site to site. The two pathways can be distinguished by: (1) amount of SO_4^{2-1} reduced relative to HCO₃ produced, (2) the δ^{13} C–DIC values; the $\delta^{13}C$ of CH $_4$ is typically ~55‰ less than that of OM, and (3) the presence or absence of other metabolites, e.g. P and N compounds, released from the OM.

The slope or linearity of SO_4^{2-} concentration profiles does not necessarily indicate that AOM is the main reaction consuming SO_4^{2-} hence, the SO_4^{2-} concentration profiles cannot be used to unambiguously calculate CH₄ fluxes. More comprehensive analyses are required to infer the dominant reactions responsible for SO_4^{2-} consumption and to estimate CH₄ flux. Furthermore, interpretation of Cl⁻ profiles, electric log response, and pressure core data show that there is no relationship between the SMT depth and GH abundance.