

# The origin and evolution of life on the methane-rich early Earth

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The long-standing paradigm for the evolution of Earth's biosphere proposes that, throughout the Earth's history, CO<sub>2</sub> from subaerial volcanism has been both the principal greenhouse gas responsible for maintaining the liquid oceans and the primary carbon source for biosynthesis, while nutrients were provided by the subaerial weathering of continental crust. However, the early oceans (before ~3.9 Ga) were likely more than twice as large in volume than today, covering nearly Earth's entire surface. Thus, the constituents of the oceans and atmosphere, including the nutrients, were more likely supplied by submarine hydrothermal fluids and minerals on the seafloor. Thermodynamic analyses of prebiotic magmatic fluids suggest that the prebiotic oceans and atmosphere were very reducing: rich in H<sub>2</sub>, CH<sub>4</sub>, and NH<sub>3</sub>, and virtually free of CO<sub>2</sub>, SO<sub>2</sub>, and O<sub>2</sub>. Thus, CH<sub>4</sub> was the principal greenhouse gas, the primary source of carbon for biosynthesis, and provided a UV shield (organic haze) for organisms. The oceans were alkaline with pH ~10 and contained very low  $\Sigma\text{Fe}$  and  $\Sigma\text{S}$  (~10<sup>-7</sup> mole/kg H<sub>2</sub>O each). Thus, methanogens and Fe- and/or S-utilizing anoxygenic phototrophs were not important. The first organisms were possibly aerobic anoxygenic phototrophic methanotrophs and oxygenic photoautotrophs (precursors of cyanobacteria) that evolved symbiotically in micro ecosystems developed on mineral surfaces by UV radiation.

The continuous subduction of hydrated and oxidized (i.e., Fe<sup>3+</sup>-enriched) oceanic crust into the mantle increased the oxidation states of the mantle and changed the volcanic gases and submarine hydrothermal fluids to be CO<sub>2</sub>- and N<sub>2</sub> rich, and decreased the ocean volume to increase the subaerial land surface area. As a result of these changes, the Earth transformed from CH<sub>4</sub>- and H<sub>2</sub>-rich to CO<sub>2</sub>- and O<sub>2</sub>-rich by ~3.9 Ga, which allowed CO<sub>2</sub>-based organisms, such as H<sub>2</sub>-, Fe- and/or S-utilizing anoxygenic phototrophs to emerge in local anoxic environments, and produced an ozone layer to shield organisms from UV radiation.

Geochemical data on Archean-aged sedimentary rocks suggest that the CH<sub>4</sub>-H<sub>2</sub> rich world was transformed to the CO<sub>2</sub>-O<sub>2</sub> rich world by ~3.9 Ga. Life may have evolved also on other methane- and water-rich planets.