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The transformation of the CH_4–NH_3–H_2-rich to CO_2–N_2–O_2-rich atmosphere occurred by ~3.9 Ga.

HIROSHI OHMOTO[1,2] AND JAMES G. FERRY[3]

[1]Penn State University
[2]The Pennsylvania State University
[3]Pennsylvania State University

Presenting Author: hqo@psu.edu

Thermodynamic analyses for compositions of the mantle, volcanic gases, submarine hydrothermal fluids, and oceans of the prebiotic Earth suggest that the life evolved in an ocean of pH =10±2 and poor in CO_2–Fe–S (< 1 µm/kgH_2O each) under a CH_4–NH_3–H_2-rich atmosphere (Ohmoto and Ferry, 2023). Therefore, CH_4, not CO_2, was the primary greenhouse gas and the principal source of carbon for early organisms.

A variety of geochemical evidence (e.g., C-, N-, S- and Pb isotopic compositions; REEs) exists to suggest that the transformation of the CH_4–NH_3–H_2-rich to CO_2–N_2–O_2-rich atmosphere, and diversification of the biosphere (e.g., phototrophic methanotrophs, oxygenic phototrophs, methanogens; sulfate-reducing bacteria, sulfur-oxidizing bacteria; oxic oceans with anoxic basins) occurred by ~3.9 Ga, due primarily to: (1) abiotic and biotic photocatalytic reactions (e.g., $H_2O + (h\nu) = H_2 + 1/2O_2$; $2CH_4 + 3O_2 + (h\nu) = (CH_2O) + CO_2 + 3H_2O$) that occurred in micro aerobic environments on surfaces of photocatalytic minerals (e.g., Pt–Ir–Cu metals, TiO_2, FeS) that accumulated as detrital minerals in shallow coastal waters on ultramafic volcanic islands; and (2) the plate tectonics which caused a continuous transfer of ocean water and the oxidized (i.e., increased $Fe^{3+}/\sum Fe$) oceanic crust into the mantle, resulting in a decrease in the ocean volume and an increase in the exposed continental surface areas, an increase in the oxidation state of the mantle to generate CO_2–N_2-rich volcanic gases, and in an increase in the nutrient fluxes to the oceans.

Current popular ideas of "oxygen oases" and "whiffs of oxygen" to explain the occurrences of oxygenated sedimentary rocks during the Archean are invalid, because the pO_2 of the atmosphere above "oxygen oases" could not have been much higher than that above the normal oceans. Alternating sedimentary units of oxic/anoxic characteristics are common in sediments that deposited in semi-closed basins (e.g., the modern Black Sea) which were invaded episodically by oxic/anoxic water bodies. The atmospheric pO_2 level has most likely remained at ~0.6 to 2 PAL since ~3.9 Ga.

Ohmoto and J.G. Ferry. The origin and evolution of life on the methane-rich early Earth, Goldschmidt Conference, 2023.