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The hydrogen, methane and ammonia biosphere on early Earth

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Abstract

Current paradigms for the origin and evolutions of life and the environment on early Earth have been based on the premises that carbon dioxide (CO_2) and nitrogen gas (N_2) were the principal constituents of the atmosphere and the sources of carbon and nitrogen for organisms today. Based on thermodynamic analyses of the redox state of the Hadean (4.56-4.0 Ga) mantle, the atmospheric compositions during the magma-ocean stage, and the effects of submarine hydrothermal fluids on the atmosphere of the ocean-covered Late-Hadean Earth, we suggest that life evolved sometime during 4.50-3.9 Ga under a reducing atmosphere, rich in hydrogen (H_2), methane (CH_4), and ammonia (NH_3), but very poor in CO_2, which was similar to today's atmosphere on Jupiter. The ocean water was alkaline (pH = 10±1) and poor in Fe^{2-} and S^{2-}. CH_4 and NH_3 were the principal sources for carbon nitrogen and energy of the first organisms, greenhouse gases, and the UV shield on early Earth. The first organisms on Earth were possibly aerobic phototrophic methanotrophs, either oxygenic and/or anoxygenic. They evolved in micro-aerobic environments, which were created by the photodissociation of H_2O on the surfaces of photocatalytic minerals

(e.g., rutile (TiO_2), pyrrhotite (FeS)) that accumulated in shallow water bodies on tropical islands. The enzymes for oxygenic Photosystem II (PSII) and PSI may also have evolved in the Late-Hadean microaerobic environments, facilitating the appearance of cyanobacteria. The symbiotic relationships between CO_2-generating methanotrophs and the CH_4-generating, H_2-oxidizing methanogens and cyanobacteria characterized the first biosphere. Plate tectonics has played a key role in the transformation of the H_2-CH_4–NH_3-rich to CO_2-N_2-rich atmosphere and biosphere by ~3.9 Ga because of the increased oxidation of the mantle, caused by the continuous subduction of the oxidized and hydrated oceanic crust into the mantle. Our study suggests that the search for life in the universe should be directed toward planets with a H_2-CH_4--NH_3-rich atmosphere, as well as to those with a CO_2–N_2-rich atmosphere. (323 words)

Key Words: Origin and evolutions of life; Methane and ammonia rich early atmosphere; Photocatalysis; Methanotrophs; Photosystem II; Cyanobacteria.

Introduction

Various geochemical and geologic data[1,2] indicate that: (i) the Earth formed through the accumulations of planetesimals and asteroids about 4.56 billion years (Ga) ago; (ii) the Earth nearly completely melted to form a magma-ocean and the core-mantle structure during 4.55-4.50 Ga; and (iii) an impact of a Mars-sized planet ejected part of the magma-ocean into space to form the Moon 4.51 Ga ago. The discovery of detrital zircon grains in Australia with isotopic ages of ~4.1-4.4 Ga and oxygen isotopic compositions ($\delta^{18}O$ = +4.5 to +8 ‰ SMOW) in ~2.7-1.8 Ga-old metasedimentary rocks suggest that the zircons were derived from a granitic magma that formed through the partial melting of oceanic crust that had been affected by an interaction with sea water[3]. These data suggest that: (i) both the ocean and continental crust developed by 4.4-4.1 Ga[3], although it is unknown how large the continental crust was and how much of it was exposed to the atmosphere; and (ii) the continental crust was exposed to the atmosphere and subjected to subaerial weathering by ~2.7 Ga. The oldest geologic formations discovered so far on Earth are the >3.7 Ga-old metamorphosed sedimentary formations in Isua, Greenland[4,5] and the ~3.9 Ga-old metamorphosed sedimentary formations in Labrador, Canada[6]. These formations include clastic sedimentary rocks (e.g., metamorphosed shales); thus, they indicate (iii) the existence of one or more land masses that were exposed to the CO_2-rich atmosphere ~3.9-3.7 Ga ago. These sedimentary rocks contain abundant kerogen (i.e., metamorphosed organic matter) with carbon isotopic compositions ($\delta^{13}C$ values) ranging from -50 to -10 ‰ PDB, which indicates (iv) the presence of a variety of organisms (possibly including cyanobacteria (CB), methanogens, and methanotrophs) in the ~3.9-3.7 Ga oceans[6-9], and (v) that life originated sometime between ~4.5 Ga and ~3.9 Ga (i.e. the Late Hadean Eon).

For life to evolve on a planet, at least the three atmospheric conditions must be established: (1) sources of carbon and nitrogen for the building-blocks of life; (2) a greenhouse gas that maintains habitable conditions; (3) the presence of liquid oceans; and (4) a shield to protect organisms from UV radiation damage. Before Holland (1984)[10], most scientists had accepted the Oparin–Urey–Miller model[11,12] as the best model for the origin of life. It postulated that the prebiotic atmosphere was very reducing (i.e., rich in H_2, CH_4, and NH_3) and that the molecular building-blocks of life were generated from mixtures of the reduced gases by electric discharge, which mimicked lightning, and/or by UV radiation. However, since Holland (1984)[10], this model has been discarded by most scientists in favor of models that postulate the origin of life from a CO_2- and N_2-rich atmosphere[10, 13-16].

Researchers have also recognized that for the nonbiological formation of the building-blocks of life from CO_2 and N_2, high-temperature ($T > \sim 200$ °C) reactions with a reductant (e.g., Fe^0, Fe^{II}) must have occurred, followed by the assembly of the building blocks to evolve organisms at ambient temperatures ($T < \sim 100$ °C). Various mechanisms/pathways for such processes have been proposed. For example, the reduction of oceanic CO_2 (H_2CO_3, HCO_3^-) and N_2 during deep circulation through ferrous-iron (Fe^{2+})-rich ultramafic rocks (e.g., peridotite) in an oceanic crust, which was followed by discharging the organic molecules into the oceans by submarine hydrothermal fluids and assembling them on the surfaces of iron sulfides (i.e., pyrrhotite (FeS), pyrite (FeS_2)) and/or serpentine near hydrothermal vents[17,18]. Zahnle et al.(2020)[19] proposed the high-temperature reduction of atmospheric CO_2 and N_2 through reactions with large iron meteorite bodies to generate the building-blocks of life.

The current paradigms[13-16] also postulate that the first primary organisms on Earth were autotrophic anaerobic chemotrophs or phototrophs that utilized CO_2, N_2 and a reductant for cell biosynthesis (CH_2O), such as H_2-oxidizing bacteria (*HOB*) that utilized H_2 from volcanic gases (i.e., $CO_2 + 2H_2 \rightarrow (CH_2O) + H_2O$), H_2S-oxidizing bacteria (Purple bacteria) that utilized H_2S from volcanic gases and/or hydrothermal fluids (i.e., $CO_2 + 2H_2S \rightarrow (CH_2O) + H_2O + 2S^0$), and Fe^{2+}-oxidizing bacteria (*FeOB*) that utilized Fe^{2+}-bearing aqueous species in the oceans and/or hydrothermal fluids (i.e., $CO_2 + 4Fe(OH)_2 + 3H_2O \rightarrow (CH_2O) + 4Fe(OH)_3$). In this article, we first evaluate the validity of the premise that CO_2 and N_2 were the principal atmospheric gases during (~4.5-3.9 Ga prior), then provide our estimates for the compositions of the prebiotic atmosphere and oceans and finally describe their influences on the origin and evolution of organisms on early Earth.

Holland's model for the prebiotic atmosphere.

The current paradigm of the CO_2- and N_2-rich prebiotic atmosphere has stemmed largely from Holland (1984)[10]. He assumed that the oxidation state of the prebiotic mantle and mantle-derived magmas was near the iron–wüstite buffer (IW: $Fe + 1/2O_2 = FeO$), which is approximately 2 logfO_2 units below the fayalite–magnetite–quartz buffer (FMQ: $3Fe_2SiO_4 + 2O_2 = 2Fe_3O_4 + 3SiO_2$) that represents the average oxidation state of the post-3.9 Ga mantle[20, 21] (Fig. 1). Applying thermodynamic data on various gas-mineral reactions, Holland[10] computed the partial pressures of magmatic gases at 1,400-1,500 K and pH_2O = 5 bar as follows: $pO_2 = {\sim}10^{-12}$ bar, $pH_2/pH_2O = {\sim}1$, $pCO_2/pCH_4 = {\sim}10^3$, $pCO_2/pCO = {\sim}1$, $pH_2S/pSO_2 = {\sim}10^4$, and $pN_2/(pNH_3)^2 = {\sim}10^3$. The ratios of partial pressures of gaseous species are essentially the same as their mole ratios. According to Holland[10], “these gases were released to the atmosphere at magmatic temperatures”. Many subsequent researchers have interpreted this statement to imply that the prebiotic atmosphere was composed of quenched magmatic gases, such that the atmospheric pO_2 was ${\sim}10^{-12}$ atm (refs. 13-16) (Fig. 1). However, there are at least three serious problems in assuming that the abundance ratios of gaseous species in the prebiotic atmosphere were the same as those of magmatic fluids at ~1,200 °C: (1) re-equilibration of volcanic gases, (2) oxidation state of the mantle, and (3) the ocean-covered Earth.

Re-equilibration of volcanic gases. Magmatic gases change their compositions due to reactions with cooler wall-rocks of the conduits as well as internal re-equilibration among the gases during cooling. This is especially true for magmatic gases from mafic/ultramafic magmas that typically degas as diffusive discharges[21, 22]. In contrast, eruptions of volcanic gases from felsic magmas, such as those formed in subduction zones, tend to be explosive and have less chance of re-equilibration[22, 23]. “Re-equilibration” is the reason why volcanologists do not directly relate the volcanic gases that were sampled at temperatures <600 °C to the magmatic compositions at ~1200 °C; instead they estimate the original magmatic fluid compositions via thermodynamic analyses of the sampled gases[22]. The paths for compositional changes of volcanic gases/fluids during reactions with the cooler wall-rocks would closely follow particular oxygen buffer lines of the rocks (e.g., FMQ, IW, and IW-2; Fig. 1)[21]. The paths for compositional changes due to re-equilibration among the gases/fluids during cooling, without any reaction with wall-rocks, would follow closely to a constant H_2/H_2O ratio of a magmatic fluid[21]. The H_2/H_2O vs. T contours nearly parallel the FMQ, IW, or IW-2 buffer lines (Fig. 1). Therefore, the cooling path for a gas mixture from an IW magma would closely follow the IW buffer line, which crosses the line of $pCO_2/pCH_4 = 1$ at ~800 °C, indicating the change from a CO_2-rich to CH_4-rich fluid at temperatures below ~800 °C; the fluid would change from N_2-rich to NH_3-rich at $T \leq$ ~400 °C (Fig. 1). Note also that the fO_2 value of the magmatic gas from an IW magma decreases from 10^{-12} bar at 1,200 °C to below 10^{-25} bar at $T \leq$ ~600 °C (Fig. 1), indicating that the idea of $pO_2 = 10^{-12}$ atm for the early atmosphere is invalid.

Recently, Miyazaki & Korenaga (2022)[23] modeled the atmospheric composition during cooling of the magma-ocean. As the magma-ocean cooled from ~1600 °C to below ~1200°C, the surface zone of the magma-ocean would have solidified, while the atmosphere continued to equilibrate with the solids down to ~250 °C(ref.23). They suggested that at the end of the magma-ocean stage at T = ~250 °C, the atmosphere was composed only of CO_2 and H_2O with P_{CO2} = ~200 atm and P_{H2O} = ~1 atm. However, this suggestion is a direct consequence of their presumption that all of the H atoms and C atoms in the Hadean mantle occurred only as H_2O and CO_2, with concentrations of 0.04-0.1 % and 200-500 ppm, respectively. They did not consider the effects of the probable presence of graphite and/or diamond (C) and pyrrhotite (FeS) in the mantle, nor the effects of the mantle redox state on the atmospheric compositions. Figs.1and 2b show that a CO_2-dominant atmosphere at T >~250 °C would have occurred only when the oxidation state of the magma-ocean, including the solidified surface zone, remained near the FMQ buffer line or higher, like the present mantle.

Oxidation state of the early mantle. The oxidation state, expressed by the fO_2 values, of the Phanerozoic mantle are around the FMQ (fayalite + magnetite and quartz) buffer[20, 21]. Most researchers agree that the fO_2 values of the Archean and the Hadean mantle were lower than the FMQ buffer, but by how much lower is still the subject of debate. For his model, Holland (1984) chose the $\log fO_2$ values of the iron-wüstite (IW) buffer, which are about two log units below those of the FMQ (Fig. 1). Most astrobiology researchers have accepted Holland's assumption. However, we have assumed the $\log fO_2$ values of the pre-4.0 Ga mantle were about 2 log units below the IW buffer line (Fig. 1) for the following reasons: (i) evaluating the effects of partitioning of Co, Cr and other elements between the core and mantle on the IW equilibrium, Wood et al. (2006)[24] concluded that the $logfO_2$ values for the pre-4.0 Ga mantle/core were approximately 2 log units below the IW buffer, and (ii) the same conclusion was obtained by Righter et al. (2020)[25] and Stagno and Fei (2020)[26] based on planetary accretion models.

The influence of submarine hydrothermal fluids on atmospheric chemistry. The volume of the Earth's ocean has been most likely decreasing throughout geologic time due to the loss of H_2O in the hydration of oceanic crust and its subduction to the mantle; the ocean volume at ~4.0 Ga was possibly more than twice that of today[27]. This would imply that the average ocean depth was greater than ~7 km, the mid-ocean ridges were more than ~5 km below sea level, and the continental crust was mostly submerged under the oceans. Exposed lands may have existed on some ocean islands where subaerial volcanism occurred, but most of the degassing from the mantle and oceanic crust was likely carried out by submarine hydrothermal fluids, rather than by subaerial volcanic gases. The pre-biotic submarine hydrothermal fluids likely developed through reactions with ultramafic rocks during the deep (>5 km) circulation of seawater through the oceanic crust, while modern submarine hydrothermal fluids develop through reaction with basaltic ocean crust[28]. After these hydrothermal fluids were discharged into the ocean, their constituents would be partitioned between the ocean and atmosphere.

Results

Chemistry of the atmosphere during the magma-ocean stage

The Late Hadean atmosphere and oceans were possibly composed of the following three components: (1) residuals of the primordial atmosphere, (2) inputs from subaerial volcanoes on oceanic islands, and (3) inputs from submarine hydrothermal fluids.

The primordial atmosphere The primordial atmosphere was created through the degassing of magmas that generated from the whole-Earth melting (i.e. the magma-ocean). Most of the gases that dissolved in the magma would have discharged into the atmosphere while cooling from ~1,600 °C to ~1,200 °C. During the cooling of the solidified magma oceans the fugacity (≈ partial pressure) ratios of magmatic gases are essentially the same as their molar ratios in the atmosphere. For the example (fCH4/fCO2) the dissolved gases Figs. 1 and 2a show the changes in the compositions of the magmatic fluids, which are the same as when in equilibrium with the cooling solidified magma-ocean with the composition of ($\log fO_2$ = IW – 2) + graphite + pyrrhotite. Fluids of ($\log fO_2$ = IW-2) would remain $CH_4 > CO_2$ at all temperatures below ~1,500 °C, and change from N_2-rich to NH_3-rich at $T \leq$ ~600 °C (Figs. 1 and 2b; Table S1). Even if the oxidation state of the mantle was as high as near the IW buffer as suggested by Holland[10], fluids from IW magmas would remain $CH_4 > CO_2$ at $T \leq$ ~1,000 °C and $NH_3 > N_2$ at $T \leq$ ~400 °C (Fig. 1), indicating that the popular idea of CO_2-N_2-rich early atmosphere[10, 13-16] is invalid.

During the cooling of the magma ocean of ($\log fO_2$ = IW-2) + graphite + pyrrhotite, concentrations of CH_4, NH_3, and H_2 would continuously increase to pCH_4 = ~10^8 atm, pNH_3 = ~10^3 atm, and pH_2 = ~10^3 atm, while the pCO_2 and pCO continue to decrease to ~10^{-10} atm at T = 250 °C, assuming that pH_2O and pN_2 were 1 atm (Fig. 1 and 2a; Table S1). The main reasons for such large increases in the pCH_4 (line CH_4(a) on Fig. 2a) were: (i) the increases of pH_2 by the reaction of ($H_2O \rightarrow H_2 + 1/2O_2$), and (ii) continuous reactions of H_2 with graphite in the solidified magma ($C + 2H_2 \rightarrow CH_4$). It was probably unlikely that the partial pressure of any gas component in the atmosphere exceeded ~1,000 atm. Therefore, the pCH_4 and pNH_3 values that exceeded ~1,000 atm at ~250 °C (line CH_4(a) on Fig. 2a) would have been converted to organic compounds (e.g., $2CH_4 + uv \rightarrow C_2H_6 + H_2$); some of the organic compounds could have remained in the atmosphere as organic haze, like the one on Saturn[29], while some deposited on the surfaces of the solidified magma oceans. If the graphite in the solidified magma was entirely consumed by the time it cooled down to ~700°C, the atmospheric pCH_4 would have remained at ~200 atm at T < ~700 °C (line CH_4 (b) on Fig. 2a), provided the solubility of CH_4 in the magma was the same as that estimated by Miyazaki & Korenaga[23] for CO_2. The atmospheric pressures of H_2S and SO_2 continued to decrease with cooling of the solidified magma ocean to pH_2S = ~10^{-7} and pSO_2 = ~10^{-20} atm at 250°C, due to the formation of FeS (i.e., $Fe + H_2S \rightarrow FeS + H_2$). The continued decreases in pCO and pCO_2 to ~10^{-9} and ~10^{-10} atm, respectively at 250°C, were due to their conversions to CH_4.

Even if the oxidation state of the mantle was as high as the IW buffer as suggested by Holland[10], the atmosphere in equilibrium with IW magma-ocean would remain $CH_4 > CO_2$ at T ≤ ~1,000 °C and $NH_3 > N_2$ at T ≤ ~400 °C (Fig. 1), indicating that the popular idea of CO_2-N_2-rich early atmosphere[10, 13-16] is invalid.

Inputs from subaerial volcanism. The gases/fluids that derived from ultramafic magmas and emitted through subaerial volcanoes on Hadean oceanic islands would have cooled along the (IW-2) buffer and discharged into the atmosphere possibly at ~1,000-600 °C as CH_4-rich gases (Fig. 2a). The addition of CH_4 to the CH_4-NH_3-H_2-rich primordial atmosphere may have promoted the production of organic compounds by photochemical reactions. Some of the organic compounds would have remained in the atmosphere as organic haze[28], while some deposited in the ocean to become proto-petroleum. However, the subaerial volcanic inputs to the prebiotic atmosphere would have been minor, since Earth's surfaces were nearly completely covered by oceans[27].

Submarine hydrothermal inputs to the Late-Hadean atmosphere. Submarine hydrothermal fluids today, and possibly throughout the geologic history of Earth, are products of seawater–rock interactions during deep (typically down to ~5-10 km) circulations of seawater through the oceanic crust[28]. Most submarine hydrothermal discharges occur at ~400-200 °C in modern systems[28], but they probably discharged at ~500-300 °C during the Late-Hadean Eon because of the hotter mantle and deeper oceans[27]; the higher water pressure of the deeper oceans allowed the higher temperature fluids to discharge into the oceans without boiling[28]. The $\log fO_2$ values of the oceanic crust during the Late Hadean were possibly elevated from the IW-2 values due to the continuous seawater-rock interactions[21]. Therefore, we have computed the compositions of the late Hadean submarine hydrothermal fluids at: (a) T = 600-200 °C, (b) pH_2O = 500 atm, (c) $\log fO_2$ = IW buffer , and (d) graphite and pyrrhotite stable (see Fig. S1 for additional assumptions). The results of these computations for the compositions of the Late-Hadean submarine hydrothermal fluids are summarized in Fig. S1, and their effects on the atmospheric compositions are presented in Table 1.

Table 1 indicates that the Late-Hadean atmosphere was rich in H_2 (i.e., pH_2 = 1,500 atm), NH_3 (i.e., pNH_3 = 520 atm), and CH_4 (i.e., PCH_4 =0.07 atm), but poor in CO_2 (i.e., pCO_2 = ~10^{-5} atm), CO (i.e., pCO = 5x10^{-5} atm), and H_2S (pH_2S = 6x10^{-6} atm), if the entire ocean water was supplied by submarine hydrothermal fluids. Note that the fugacity values of CO_2, and CO are independent of fH_2O, but those of CH_4, H_2, H_2S, SO_2, and $(NH_3)^2/N_2$ increase with increasing fH_2O. Note also that if the total amount of submarine hydrothermal fluids was 1/10 of the total mass of the Late-Hadean ocean, then the partial pressures of H_2, NH_3, CH_4, and H_2S in the atmosphere would become 1/10 of the values presented in Table 1 (e.g., pH_2 = 150 atm, pCH_4 = 0.007 atm, pNH_3 = 5 atm). Table 1 also shows that the compositions of the late-Hadean atmosphere were similar to those of today's atmosphere on Jupiter[31], except for the pH_2O values, which reflect the large difference in the surface temperature (i.e., 25°C for the Hadean Earth vs ~ -110°C for Jupiter): the $pH_2O(v)$ value in equilibrium with liquid water at 25°C is 0.03 atm, whereas the $pH_2O(v)$ <<<0.1 atm when in equilibrium with ice at -110°C. Some planets of the outer Solar system, Titan, Uranus, and Neptune, also have atmospheres with ~1-4 % CH_4 and more than 80% H_2(ref.32) .

Based on the results of these computations, we conclude that the atmosphere of the first biosphere (~4.50-4.0 Ga) was rich in H_2, CH_4 and NH_3, and poor in CO_2, CO, and H_2S, regardless of the proportions of the residual primordial atmosphere and that the atmosphere originated from submarine hydrothermal fluids.

Chemistry of the Prebiotic Oceans. From an assemblage of siderite ($FeCO_3$) + minnesotaite ($Fe_3Si_4O_{10}(OH)_2$), a common mineral assemblage in banded-iron formations (BIFs), Ohmoto et al. (2004)[33] estimated via thermodynamic analyses that, during the ~3.8-1.8 Ga period when the major BIFs formed, the atmospheric pCO_2 was ≥ ~0.05 atm (i.e., >100 times the present atmospheric level of ~400 ppm) and the oceanic pH was ~7 (compared to 8.1 today). In contrast, according to our calculations, CO_2 was virtually absent in the prebiotic atmosphere and oceans (Figs. 1 and Table 1). Therefore, the pH of the prebiotic oceans was not controlled by the CO_2 - carbonate equilibrium as today. Instead, the concentrations of H^+, Fe^{2+}, $\sum Fe^{2+}$, $H_2S_{(aq)}$, and $\sum S^{2-}$ in the prebiotic oceans were most likely controlled by the equilibria with the alteration minerals produced by submarine hydrothermal fluids and submarine weathering of the ultramafic oceanic crust, namely serpentine minerals and ferrous-iron hydroxide ($Fe(OH)_{2(s)}$), together with the residual primary pyrrhotite (FeS) (Figs. 3a and -b). The pH values were probably within 10±1, as suggested from the typical pH values of hot spring waters (both subaerial and submarine) in serpentine-rich rocks[34-38]. Concentrations of Fe^{2+}-rich aqueous species (Fe^{2+}, $Fe(OH)_{2(aq)}$, $Fe(OH)^+$, $Fe(OH)_3^-$, and $\sum Fe^{2+}$) in solutions in equilibrium with $Fe(OH)_{2(s)}$ at 25 °C suggest a$\sum Fe^{2+}$ content of around 10^{-8} moles/kg H_2O at pH = ~10 (Fig. 3b). Additions of Fe-chloride complexes (e.g., $FeCl^+$, $FeCl_2$) at $\sum Cl$ = ~1 moles/kg H_2O, and increasing the temperature to 50 °C, may increase the $\sum Fe^{2+}$ content to ~10^{-6} moles/kg H_2O. The concentrations of ferric-iron (Fe^{3+})-bearing species were negligible in the O_2-free oceans[39]. The concentration of $\sum S^{2-}$ species in the oceans at pH = 10±1 would be ~$10^{-7\pm1}$ moles/kgH_2O (Fig. 3b). Results of these calculations, therefore, indicate that the suggestions made by many researchers[14-16] of Fe^{2+}- and/or H_2S-rich (i.e., > ~10^{-3} moles/kg H_2O) early oceans are invalid.

Discussion

The First Biosphere on Earth

Results of our computations on compositions of the prebiotic atmosphere and ocean suggest that CH_4 and NH_3 were the principal sources of C and N for the biosynthesis of cell material and energy conservation for autotrophic organisms, the greenhouse gases, and the UV shield on early Earth. UV photolysis of CH_4–NH_3-rich and O_2-poor atmosphere would have produced organic haze[40] and proto-petroleum with a variety of organic compounds, much like those of Titan's atmosphere[29], for the greenhouse and ozone- shield. Our suggestions for the geological and geochemical environments for the first biosphere are schematically illustrated in Fig. 4.

Methanotrophs. Because the late-Hadean atmosphere contained virtually no CO_2, but was rich in H_2, CH_4 and NH_3, the first organisms to evolve on Earth were most likely those that utilized these reduced compounds, such as methanotrophs (methane oxidizing bacteria (MOB) and ammonia oxidizing bacteria (AOB). MOB are from the domains *Bacteria* or *Archaea*, chemotrophic or phototrophic, and aerobic or anaerobic[41]. In this article we will not discuss AOB (i.e., chemotrophs), because our focus is on the evolution of phototrophs. Ancestral (primitive) MOB may or may not have had the same set of genes, morphologies, and biochemical functions as those of modern day, however, the basic requirements for the ancient *MOB* would have been the same as the modern ones. For organisms that utilize CO_2 and N_2 as the primary constituents for biosynthesis, a reductant (e.g., H_2, H_2S, Fe^{2+}) is needed. In contrast, for organisms that utilize CH_4 and NH_3 in biosynthesis, an oxidant is needed. Common environments for MOB are stratified water bodies, where aerobic water is underlain by an anaerobic water body (e.g., basin). CH_4 is generated in the anoxic water body by methanogens that utilize the detritus of autotrophic- and heterotrophic organisms *via* the reaction $2(CH_2O) \rightarrow CO_2 + CH_4$. In the upper aerobic water layer, the CH_4 which migrated upward from the lower anoxic water is consumed by aerobic methanotrophs that utilize O_2 from the atmosphere and/or those produced locally by cyanobacteria (R2). In the lower anoxic water bodies, CH_4 is oxidized by anaerobic chemotrophic MOB that utilize other oxidants, such as SO_4^{2-}, NO_3^-, and $FeOOH_{(s)}$ (R3-R5) singularly or in collaboration with partner microbes:

$$CH_4 + O_2 \rightarrow (CH_2O) + H_2O \qquad \text{(R2)}$$

$$2CH_4 + SO_4^{2-} + H^+ \rightarrow 2(CH_2O) + HS^- + 2H_2O \qquad (R3)$$

$$5CH_4 + 4NO_3^- + 4H^+ \rightarrow 5(CH_2O) + 2N_2 + 7H_2O \qquad (R4)$$

$$CH_4 + 4FeOOH_{(s)} + H_2O \rightarrow (CH_2O) + 4Fe(OH)_{2(s)} \qquad (R5)$$

in which (CH_2O) represents cell biomass. The oxidants for the chemotrophic *methanotrophs* (e.g., SO_4^{2-}, NO^3-, $FeOOH_{(s)}$) are produced by the oxidative weathering of reduced compounds (e.g., N-bearing organic compounds, ferrous-rich minerals, sulfide minerals) under an O_2-rich atmosphere, such as:

$$4FeS_{(s)} + 9O_2 + 6H_2O \rightarrow 4FeOOH_{(s)} + 4SO_4^{2-} + 8H^+ \qquad (R6)$$

Therefore, in open-oceans under the O_2-free early atmosphere, both aerobic *MOB* and anaerobic MOB would have been unimportant. Methanotrophs that were discovered in hydrothermal vents[42] utilized CH_4 from hydrothermal fluids and O_2 in deep ocean water in biosynthesis via R2. However, such a scenario was not applicable to the MOB on the Hadean Earth, because the deep ocean water, as well as the shallow open oceans, were devoid of O_2 (Fig. 1).

MOB coexist with cyanobacteria in shallow water bodies that overly CH_4-rich anoxic water bodies in many European lakes[43-4]. Such relationships suggest that the *MOB* utilize the CH_4 from the underlying anoxic water bodies and the O_2 generated locally by the coexisting cyanobacteria, rather than by utilizing the atmospheric O_2 for oxidizing CH_4; that is, the MOB and cyanobacteria were in symbiotic relationships. An important question was whether the MOB in such an aerobic environment were chemotrophs or phototrophs. Through genomic analyses, researchers have found that these MOB have the genes involved in phototrophy (*bchBCDEGHIJNLMNOPXYZ, acsF, pufABCML)* as well as those responsible for methane oxidation (e.g., *particulate methane monooxygenase* (*pMMO*), *soluble methane monooxygenase* (*sMMO*), *methanol dehydrogenase* (*mxaF*))[43-48]. Some of the phototrophic genes are those that encode Photosystem II (PS-II), which is an enzyme complex that catalyzes the photodissociation of H_2O to O_2 and electrons (i.e., R7) in modern oxygenic phototrophs (e.g., cyanobacteria). However, these MOB do not generate O_2 [43-48]. Thus, they are termed aerobic anoxygenic phototrophic methanotrophs (AAPM)[43-48]. Researchers have debated if PS-II of the ancient AAPM were oxygenic but lost their ability to split H_2O due to lateral gene transfers or for unknown reasons during their evolution[43-48]. Considering this, we suggest the possibility that PS-II of the ancestral AAPM was able to split H_2O; that is, they were aerobic oxygenic phototrophic methanotrophs (AOPM):

$$2H_2O + h\nu + (\text{PS-II}) \rightarrow O_2 + 4H^+ + 4e^- \rightarrow O_2 + 2H_2 \qquad \text{(R7a)}$$

The O_2 generated by PS-II would be used to oxidize atmospheric CH_4 for a carbon and energy source for the AOPMs:

$$CH_4 + H_2O + h\nu + (\text{PSII}) \rightarrow (CH_2O)_{\text{AOPM}} + 2H_2 \qquad \text{(R7b)}$$

and $$2CH_4 + 4H_2O + h\nu + (\text{PSII}) \rightarrow (CH_2O)_{\text{AOPM}} + HCO_3^- + H^+ + 6H_2 \qquad \text{(R7c)}$$

Questions remain regarding the temporal and genetic relationships between the AAPM and the AOPM. One possibility is that they evolved together. Another possibility is that the increased availability of abiotically-generated O_2 (e.g., by photocatalytic minerals; see below) could have caused the PSII of the AOPM to gradually lose their necessity and ability to split H_2O and therefore transformed to AAPM.

Microaerobic environments – Cradles of life. In efforts to utilize the H_2 that generated from the photodissociation of H_2O by sunlight as an alternative energy source, recent researchers have discovered many photocatalytic minerals and metals that significantly increase the rates of photochemical reactions[49-52], such as rutile (TiO_2), ilmenite ($FeTiO_3$), pyrrhotite (FeS), serpentine (Fe-Mg-rich clays), and Pt-, Ir-, and Cu-metals:

$$2H_2O + h\nu + (\text{photocatalyst}) \rightarrow O_2 + 4H^+ + 4e^- \rightarrow O_2 + 2H_2 \qquad \text{(R7d)}$$

We propose that the first methanotrophs utilized the molecular O_2 that generated in a micro-aerobic layer, perhaps a few millimeters in thickness, which developed on the surfaces of photocatalytic minerals that were derived from ultramafic rocks (e.g., peridotite) and accumulated in shallow (<~2 m) water bodies (e.g., lagoons) on tropical ocean islands (Figs. 4, 5). Because the H_2 from R7d escaped faster than O_2 to the space, the mineral surfaces and their vicinities would have become micro-aerobic environments.

Thus, the AOPM that utilized O_2 generated by PSII were probably not the only type of MOB that existed in the micro-aerobic environments. The O_2 generated by photocatalytic minerals (R7d) could have been used directly by the AAPM *via* R2 (Fig.5). Furthermore, the O_2 generated on photocatalytic mineral surfaces may have been used to oxidize sulfide- and Fe^{2+}-bearing minerals to generate SO_4^{2-} and $FeOOH_{(s)}$, which may have been used to oxidize CH_4 for energy conservation and biosynthesis via R3-R6 through reversal of the pathway in present-day methanogens. Indeed, the methanogen *Methanosarcina acetivorans* is capable of methanotrophic growth dependent on reduction of Fe(III) (Yan et al., 2023)[53]. We propose that present-day methanogens and ANME (ANaerobic MEthanotrophic) microbes evolved from these ancient anaerobic methanotrophs. The H_2 from the Hadean atmosphere and those generated by the photocatalysis of H_2O, together with CO_2 generated by MOB, could have facilitated the evolution of H_2-oxidizing bacteria (HOB), possibly including cyanobacteria. MOB and HOB in symbiosis probably formed a benthic microbial mat on the surfaces of catalytic-minerals (Fig. 5). When this microbial mat was overlain by a new layer of photocatalytic minerals, the environment for the early microbial mat would have changed to anaerobic, allowing evolution of anaerobic microbial food chains to produce CO_2 and CH_4 utilizing organic matter derived from microbial detritus in the microbial mat. The generated CO_2 and CH_4, which migrated upward and were used to generate a new benthic mat on the surfaces of new photocatalytic minerals (Fig. 5).

The microaerobic environment that developed on mineral surfaces offered another advantage over an open ocean for providing the essential elements in photosynthesis, such as Fe and S in the PSI reaction center, Mn in the PSII reaction center, and Mg and Ca in chlorophyll, because the microbes in the microaerobic environments could have easily obtained these bio-essential elements from the underlying catalytic minerals (e.g., FeS, MnS, MnS, serpentine).

UV photocatalysis on early Earth. UV photocatalytic reactions would have been much more intensive and extensive on early Earth compared to today for the following reasons: (i) Although the solar flux on the early Earth was much less than today[54, 55], the UV flux from the young sun was likely much higher than today, possibly more than 10 times higher at ~4.**2** Ga[ref.56] (Fig. 6). (ii) The rates of UV photolysis generally increase with increasing OH^- contents of water[57, 58], making the UV-induced reaction rates much higher in early oceans of pH = 10±1 compared to today's oceans of pH = 8.1. (iii) The conversion of CH_4 to CO_2 in the presence of H_2O and photocatalytic minerals was greatly accelerated as methanol (CH_3OH) and/or formic acid (HCOOH) were added[59]. For example, in the experiments using a Cu/TiO_2 photocatalyst, an addition of 1% methanol to H_2O increased the H_2 production rate by ~30 times (from ~0.15 moles H_2/hr/gram of the minerals to ~5 moles H_2/hr/gm minerals)[59]. Because methanol and formic acid are produced during the photocatalysis of CH_4 and H_2O, they become auto catalysts for the photocatalysis of CH_4 (R4). Recent studies to find effective photocatalytic methods to clean up polluted CH_4-rich water bodies (e.g., sewage waters) have recognized rapid formations of a variety of carbohydrates[59-61] and amino acids[62, 63] from CH_4-rich solutions of pH = ~10, compared to CH_4-and NH_3-free waters.

Evolution of phototrophic organisms. If AOPM*s* were the earliest microbes with oxygenic PSII, then photosystem I (PSI) essential for microbes that utilized H_2 and CO_2 in biosynthesis (e.g., HOB), could have also evolved in micro-aerobic environments (Fig. 5). Likewise, cyanobacteria that needed both PSII and PSI may have also evolved in the same environments. We are aware that this interpretation contradicts the current paradigms of microbial evolution. Common beliefs among geologists[13-16] and biologists[63-66] have been that: (i) CO_2-utilizing anaerobic anoxygenic phototrophic and/or chemolithotrophs (e.g., HOB, purple bacteria, and FeOB) were the first organisms that evolved by ~3.9 Ga; (ii) cyanobacteria evolved at ~3.2. Ga ago; (iii) aerobic microbes, including aerobic *MOB*, evolved after the atmosphere became O_2-rich (i.e., “the Great Oxygenation Event” at ~2.5 Ga); (iv) methane oxidizing chemotrophs which couple with the reduction of NO^{3-}, SO_4^{2-}, NO_3^- or $FeOOH_{(s)}$ evolved after the oceans became rich in theses oxidants around ~2.4 Ga; (v) since HOB, purple bacteria and other anaerobic phototrophs utilize only CO_2 and PSI in biosynthesis, but cyanobacteria need PSII as well as PSI, PSI must have evolved before PSII. However, based on genomic analyses of PSI and PSII, Cardona[68, 69] suggested that PSII evolved before PSI. Our analyses of the Hadean atmosphere and of the microaerobic environments suggest the possibility that PSII evolved first in the micro-aerobic environments, which was closely followed in time and space by the evolution of PSI that was utilized by HOB (Fig. 5). The evolutions of both oxygenic PSII and PSI led cyanobacteria to evolve. Thus, the first biosphere was comprised of AOPM, AAPM, HOB, purple bacteria, FeOB, cyanobacteria, and methanogenic consortia that flourished symbiotically.

Transformation of the CH_4–NH_3–H_2-rich to CO_2–N_2–O_2-rich atmosphere. On early Earth, photocatalytic reactions in the micro-aerobic environments converted H_2O, CH_4, and NH_3 into CO_2, N_2, O_2 and H_2, as well as CH_2O (Fig. 5). Some of the CO_2 and O_2 that generated in the microaerobic environments spread to the open oceans and atmosphere to gradually transform the CH_4–NH_3–H_2-rich to a CO_2–N_2–O_2-rich atmosphere (Fig. 6). However, photocatalytic processes alone could not have caused this transformation if CH_4-, NH_3- and H_2-rich gases were continuously supplied by submarine hydrothermal fluids. To completely transform the atmospheric chemistry, the inputs from the mantle to the atmosphere must have changed to CO_2- and N_2-rich (Fig. 1). This would have required a decrease in oceanic volume and an increase in the air-exposed continental surfaces, to increase the oxidation state of the mantle to near the FMQ buffer, and to change the mantle degassing mode from submarine hydrothermal fluids to continental volcanic gases (see Figs. 1 and 2b). Such changes would have required plate tectonics, which caused continuous subduction of the hydrated- and oxidized (i.e., increased $Fe^{3+}/\sum Fe$ ratio) oceanic crust into the mantle[21].

The oldest sedimentary rocks on Earth are ~3.7-3.9 Ga metasedimentary rocks and banded-iron formations (Bis) in Labrador, Canada[6]. We suggest that the transformation from a CH_4–NH_3–H_2-rich to CO_2–N_2-O_2-rich atmosphere occurred at about ~3.9 Ga because of the following and other lines of evidence: (i) From thermodynamic analyses of the conditions for the abundant siderite ($FeCO_3$) and goethite (FeOOH) in the 3.9 Ga BIFs in Isua and the 3.5-1.8 Ga BIFs in the world, Ohmoto et al (2004)[33] suggested the ~3.9-1.8 Ga atmosphere was rich in CO_2 (i.e., $pCO_2 \geq 0.04$ atm : more than 100 times higher than the present atmospheric pCO_2 value of ~400 ppm) and poor in CH_4 (i.e., $pCH_4 < 100$ ppm). (ii) Metasediments in Isua are characterized by abnormally high isotopic ratios of $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$, indicating that the sediments deposited in a U-enriched ocean[4], which is an indication of the oxidative weathering of UO_2 on land. (iii) Rare-earth element patterns of the 3.8 Ga BIFs in Isua BIFs[5] and the 2.9-2.7 Ga BIFs in India[70] are characterized by distinct negative Ce anomalies, which is strong evidence for an oxygenated atmosphere and oceans. (iv) Enrichments of $Fe^{3+}$and depletions of Fe^{2+}in modern soils, which were produced by organic acids that derived from the decay of terrestrial biota under an oxygenated atmosphere, are commonly observed in paleosols 2.9-2.2 Ga in ages[71]. (iv) The presence of mass-independent fractionation of sulfur isotopes (MIF-S) in many (not all) sedimentary rocks older than ~2.4 Ga has been used by many geologists[13-16] as indisputable evidence for an anoxic Archean atmosphere. However, Ohmoto (2020)[21] discussed that the MIF-S signatures in sedimentary rocks were most likely produced by SO_4^{2-}-rich ocean water via: (a) the involvement in explosive volcanism and UV-photochemical reactions in the O_2-rich stratosphere involving SO_2 gas from SO_4^{2-}-rich magmas, and/or (b) high-temperature (~150 °C) reactions with immature organic matter in sediments. An important reason for the frequent occurrences of MIF-S in pre-2.4 Ga sediments was because the UV fluxes were many orders of magnitudes higher than today (Fig. 6). SO_4^{2}-rich ocean is created by O_2-rich atmosphere. Therefore, the MIF-S is, in fact, the best evidence for an oxygenated atmosphere through the Archean and younger times.

Summary and Conclusions

The major differences between the current paradigms and our suggestions for the origin and evolutions of life and environments are summarized in Table 2.

Important suggestions from this study include the following:

(1) The pre-biotic atmosphere was most likely CH_4–NH_3–-H_2-rich and CO_2–N_2–-O_2-poor. Therefore, the Oparin–Urey–Miller model for the origin of the building blocks of life is valid; the current paradigm for the origin and evolution of life from a CO_2–N_2-rich atmosphere is invalid.

(2) The CH_4–NH_3-H_2-rich and CO_2-N_2-O_2-poor pre-biotic atmosphere and oceans were created because: (a) the oxidation state (i.e., the fO_2 values) of the mantle and the mantle-derived magmas on early Earth was approximately 2 log units lower than those of the Iron–Wustite (IW) buffer, and (b) the prebiotic Earth was nearly completely covered by the oceans, causing the

degassing into the oceans and atmosphere to have occurred mostly by submarine hydrothermal fluids that circulated through oceanic crust with ($\log fO_2$ = ~IW) + graphite + pyrrhotite at ~300-500°C.

(3) The pre-biotic oceans were poor in $\sum Fe^{2+}$, $\sum S^{2-}$ and $\sum CO_2$. Therefore, the current paradigm, which postulates that the first organisms on Earth were anoxygenic chemotrophs (and/or phototrophs) that utilized H_2, Fe^{2+} or S^{2-} to convert CO_2 to CH_2O is invalid.

(4) The first organisms to appear on Earth were possibly aerobic oxygenic phototrophic methanotrophs (AOPM) and/or aerobic anoxygenic phototrophic methanotrophs (AAPM*)* that evolved in micro-aerobic environments, which were created on surfaces of photocatalytic minerals (e.g., Pt, FeS, TiO_2, and serpentines) under the H_2-, CH_4- and NH_3-rich atmosphere. These minerals were detrital minerals from ultramafic rocks on oceanic islands and accumulated in shallow coastal water bodies.

(5) The important elements used in photosynthesis, such as Mn in PSII, Fe-S clusters in PSI, and Mg in bacteriochlorophylls, were obtained mostly from the photocatalytic minerals, rather than from the normal ocean water.

(6) Microbes that utilized CO_2 and H_2 (e.g., HOB, possibly including cyanobacteria) and methanogenic consortia also evolved in micro-aerobic environments.

(7) The higher UV flux from the early sun and higher pH (~10) ocean water under the CH_4- and NH_3-rich atmosphere, compared to today, promoted the photocatalytic reactions that are vital for the origin and evolutions of life and the environments on early Earth.

(8) The higher UV fluxes in the oxic stratosphere were mostly responsible for the frequent occurrences of MIF-S signatures in pre-2.4 Ga sedimentary rocks.

(9) The search for life in the Universe should be directed towards planets with CH_4–H_2–NH_3-rich atmospheres, as well as to those with CO_2–N_2-rich atmospheres. (6,284 words)

Methods

Thermodynamic computations for the compositions of the mantle, mantle-derived magmas, volcanic gases, submarine hydrothermal fluids, and the oceans on early Earth were performed using the equilibrium constants summarized in Tables S1 and S2.

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Data Availability

All data generated and analyzed during this study are included in this published article and its supplementary information files.

Figure legends

Fig. 1. Stability relationships of minerals and gaseous species as a function of temperature and O_2 fugacity. H: hematite (Fe_2O_3), M: magnetite (Fe_3O_4), F: fayalite (Fe_2SiO_4), Q: quartz (SiO_2), W: wüstite (FeO), I: iron (Fe). MH: magnetite + hematite buffer, FMQ: fayalite + magnetite + quartz buffer, IW: iron + wüstite buffer, and IW-2: IW buffer values minus $2\log fO_2$. Prebiotic mantle (I): the values adopted by Holland (1984)[10]. Prebiotic magmas (II): the values adopted in this study. The conditions for $CO_2/CH_4 = 1$, $H_2O/H_2 = 1$, and $N_2/(NH_3)^2 = 1$ are shown by red-, blue-, and brown lines, respectively. The values were computed using thermodynamic data in Table S2.

Fig. 2. Compositions of the fluids in equilibrium with cooling volcanic rock. (a). Compositions of the atmosphere in equilibrium with the cooling magma-ocean. Line CH_4(a) is when graphite existed at all temperatures. Line CH_4(b) is when graphite was exhausted at T = 700 °C. The fCH_4, fNH_3, and fH_2 values above ~1,000 bar may have been reduced to <1,000 bar by the formation of organic compounds (e.g., organic haze, proto-petroleum). (b) Compositions of gases from typical volcanoes associated with modern subduction zones. Note the contrasts in the fluid compositions between (a) and (b): the fluids from a reducing magma are rich in reduced compounds (CH_4, NH_3, H_2) and poor in CO_2, whereas those from an oxidized magma are rich in CO_2, but poor in the reduced species.

Fig. 3. Compositions of the prebiotic oceans. (a): Phase diagram of minerals in the Fe-O-S system with C(graphite)-CO_2-CH_4 at 25°C. The green area represents the fO_2 conditions for the formation of cells of organisms. The early biosynthesis was carried out mostly by the oxidation of CH_4 (red arrow), while the modern biosynthesis by the reduction of CO_2 (black arrow). (b):Concentrations of Fe^{2+}- and S^{2-}-bearing aqueous species in equilibrium with $Fe(OH)_{2(s)}$ and FeS at 25 °C. The values were computed using thermodynamic data in Table S3.

Fig. 4. A schematic illustration of the geological and geochemical characteristics of the pre-biotic Earth. The important characteristics include: the nearly-completely ocean-covered Earth; the continental crust mostly submerged in the oceans; the degassing of gases/fluids to the oceans mostly by reducing submarine hydrothermal fluids; the H_2–CH_4–NH_3-rich atmosphere; the Fe–S–H^+-poor oceans; the origin and evolution of life on ocean islands; and an organic haze layer for the protection of life from UV radiation from the sun.

Fig. 5. Schematic illustration of the chemical, biological, and mineralogical components in a micro-aerobic environment for the Cradle of life. AAPM, aerobic anoxygenic phototrophic methanotroph. AOPM, aerobic oxygenic phototrophic methanotroph. AAPM and AOPM oxidized methane derived from the atmosphere or produced by methanogenic microbial consortia. HOB, H_2-oxidizing bacteria. O_2 internally generated by PSII of AOPM (blue arrow) were utilized by the AOPM, and O_2 externally generated by photocatalytic minerals derived from ultramafic rocks (black arrow) were utilized by the AAPM. PSI and HOB also evolved on the surface of detrital minerals of the micro-aerobic environment (yellow arrows) utilizing H_2

derived from photocatalysis or the atmosphere. CB, cyanobacteria that evolved by utilizing PSII and PSI (green). AOPM, AAPM, HOB, CB and methanogenic microbial consortia derived essential inorganics from ultramafic rocks.

Fig. 6. The changes in the solar luminosity and UV flux throughout Solar history.

Tables

Table 1. The influence of submarine hydrothermal fluids on the Late-Haden atmosphere. See Fig. S1 for the adopted assumptions. The Henry's constants are from Sander (2015)[30].

	Fugacity of species in 400 °C hydrothermal fluids (atm)	Mole ratio (*mi/m*CH_4) of hydrothermal specie	Henry's constant (P*i*/m*i*) at 25 °C	Partial pressure of atmospheric specie at 25 °C (atm)	Mole ratio (*mi/m*CH_4) in the Hadean atmosphere	Mole ratio (*mi/m*CH_4) in Jupiter's atmosphere
H_2O	$10^{1.7}$	$10^{3.8}$	3×10^{-2}	0.03	0.4	<<<1
H_2	10^{3}	$10^{5.1}$	$1.3 \text{x} 10^{3.}$	$1.5 \text{x} 10^{3}$	$2 \text{x} 10^{4}$	480
CH_4	$10^{-2.1}$	1	$7.0 \text{ x} 10^{2}$	$7 \text{x} 10^{-2}$	1	1
CO_2	$10^{-4.8}$	$10^{-2.7}$	3.0x10	$1.1 \text{x} 10^{-5}$	10^{-4}	10^{-6}
CO	$10^{-4.4}$	$10^{-2.3}$	$1.0 \text{x} 10^{3}$	$5 \text{x} 10^{-5}$	$7 \text{x} 10^{-4}$	$8 \text{x} 10^{-7}$
H_2S	$10^{-1.7}$	$10^{0.4}$	9.8	$6 \text{x} 10^{-6}$	$9 \text{x} 10^{-3}$	$3 \text{x} 10^{-3}$
N_2	10^{-2} (*assumed)	1	$1.5 \text{x} 10^{3}$	$1.5 \text{x} 10^{-2}$	2	?
NH_3	$10^{1.6}$	$10^{3.6}$	$1.6 \text{x} 10^{2}$	5.2x10	$7 \text{x} 10^{2}$	$3 \text{x} 10^{-1}$
He						76

Table 2. Comparison of the current paradigms *vs* the suggestions made in this paper for the geochemical and biological environments and processes on early Earth.

Topics	**Current paradigms**	**This paper**
Oxidation state of the Hadean mantle	log fO_2 = Iron/Wüstite (IW) buffer	logfO_2 = IW - 2
Major constituents of the atmosphere during the magma-ocean stage (4.56-4.50 Ga)	CO_2 & H_2O	H_2, CH_4, NH_3
Major constituents of the Late-Hadean (4.50-4.0 Ga) atmosphere	CO_2, N_2	CH_4, NH_3, H_2
Major sources for the Late-Hadean atmospheric gases	Subaerial volcanic gases	Submarine hydrothermal fluids
Compositions of the Late-Hadean oceans	pH = 7-8 rich in Fe^{2+} & H_2S	pH = 10±1 poor in Fe^{2+} & H_2S
Sources of methane in the Late-Hadean atmosphere	Methanogens	Submarine hydrothermal fluids
Main green-house gases in the Late-Hadean atmosphere	CO_2 + minor CH_4	CH_4 & NH_3 (organic haze)
UV shield for organisms in the Late-Hadean atmosphere	Organic haze	Organic haze
First organisms	Evolved before 3.9 Ga H_2-oxidizing bacteria (*HOB*) Fe^{2+}-oxidizing bacteria (*FeOB*) S^{2-}-oxidizing *Purple bacteria* *Methanogens*	Evolved during 4.50-4.0 Ga *Aerobic oxygenic phototrophic methanotrophs* (AOPM), *Aerobic anoxygenic phototrophic methanotrophs* (*AAPM*), *HOB, Cyanobacteria, Methanogens*
Time of the first appearance of cyanobacteria	~3.0 Ga	~4.5-3.9 Ga
Time of the first appearance of methanotrophs	After the GOE (~2.4 Ga)	~4.5-3.9 Ga
Photosystems (evolution)	*PSI* (earlier)® *PSII* (later)	Emergence of *PSII* & *PSI* together; losses of some genes for H_2O dissociation from *PSII* during evolution
Sources of metals in photosystems	Seawater	Photocatalytic minerals
Origin of CO_2-rich atmosphere	Hadean (>3.9 Ga), volcanic gases	Archean (<3.9 Ga) plate tectonics
Causes of MIF-S in sedimentary rocks	UV photolysis of volcanic SO_2 in an anoxic troposphere	Photolysis of volcanic SO_2 in an oxic stratosphere under high fluxes of UV