

Research

Serpentinite and the dawn of life

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Submarine hydrothermal vents above serpentinite produce chemical potential gradients of aqueous and ionic hydrogen, thus providing a very attractive venue for the origin of life. This environment was most favourable before Earth's massive CO₂ atmosphere was subducted into the mantle, which occurred tens to approximately 100 Myr after the moon-forming impact; thermophile to clement conditions persisted for several million years while atmospheric pCO₂ dropped from approximately 25 bar to below 1 bar. The ocean was weakly acid (pH ~ 6), and a large pH gradient existed for nascent life with pH 9–11 fluids venting from serpentinite on the seafloor. Total CO₂ in water was significant so the vent environment was not carbon limited. Biologically important phosphate and Fe(II) were somewhat soluble during this period, which occurred well before the earliest record of preserved surface rocks approximately 3.8 billion years ago (Ga) when photosynthetic life teemed on the Earth and the oceanic pH was the modern value of approximately 8. Serpentinite existed by 3.9 Ga, but older rocks that might retain evidence of its presence have not been found. Earth's sequesters extensive evidence of Archaean and younger subducted biological material, but has yet to be exploited for the Hadean record.

Keywords: RNA world; origin of life; Hadean; Archaean; anoxygenic photosynthesis; serpentinite

1. INTRODUCTION

The inevitable interaction of the nascent hydrosphere with mantle rocks produced viable geochemical niches for the origin of life. Possible association of hydrothermal vents with the origin of life is notorious, with deeply rooted conserved biochemistry being compatible with this hypothesis (e.g. [1–6]). Fe, Mg and Mn are expected in such vent waters, but are too abundant in many common rock types to provide specific information of geological environments. Alternatively, the widespread use of sulphur by life is a traditional starting point of hydrothermal discussions (e.g. [5,7,8]), and related arsenic resistance biochemistry exists in Archaea and Bacteria [9]. Zinc has also been implicated as a nascent biological element [10,11]. These elements provide little information of the ecological niches at the *dawn of life*.

Other minor and trace elements are more revealing to specific rock types. Mantle-derived serpentinite and komatiite are rich in Ni and Co (see §3c for petrology). The presence of Ni in methanogens and Co in the RNA cofactor B-12 indicates these rocks are ancestral homes (e.g. [12,13]). Ribose, a building block of RNA, may form spontaneously in serpentinite fluids with borate ions stabilizing ribose from becoming tar [14,15].

In this paper, we focus on the environmental niches provided by 'white-smoker hydrothermal vents' above serpentinite as a possible pre-biotic venue. Lane

et al. [16] and Russell *et al.* [6] presented a geologically detailed sequence of events leading to origin of life. Here, we concentrate on tractable Earth science issues: specifically the timing and 'inorganic' aspects of chemistry where rocks and ambient fluids modulate complex organic processes. In particular, the most favourable pre-biotic environment, that includes a high-pCO₂ and sea water of pH ~ 6 above an ocean floor serpentinite, was transient in early Earth history, lasting only several million years. We refer the reader to reviews of macromolecular chemistry in geological contexts by Cleaves & Lazcano [17] and Russell & Hall [5] and the important role of viruses on the early Earth by Koonin & Martin [18] and Brüssow [19].

2. SERPENTINITE ORIGIN OF LIFE

Viable ecological niches are formed by the reaction of hydrothermal sea water with mantle rocks to form serpentinites and the subsequent reaction of the vent fluids with CO₂-bearing sea water. Lane *et al.* [16] and Russell *et al.* [6] were geologically explicit: life originated around alkaline (pH 9–11) vents from serpentinite on the seafloor. The sulphide-rich and Ca²⁺-rich fluid precipitated iron sulphides on contact with Fe²⁺-bearing anoxic sea water and CaCO₃ on contact with CO₂ in sea water, forming a micrometre-scale pore space. Travertine on terrestrial (continental) springs is grossly similar.

In addition to physical confinement, the vent chimneys contained Fe-, Ni- and S-bearing minerals that acted as organic catalysts. Metal clusters in extant organisms are likely pre-RNA relicts in this hypothesis. Percolation of fluids through honeycomb pore networks concentrated nucleotide molecules and eventually

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nucleic acid chains [5,20], thus providing conditions favourable for life's origins [21]. Recirculation through locally high thermal gradients in the porous networks further concentrated nucleic acids and lipids [22].

The initial organism envisioned by Lane *et al.* [16] and Russell *et al.* [6] was cloistered within pore spaces having lipid-lined rock acting like a cell membrane. It evolved from using RNA to using DNA as its genetic material. That is, the last universal common ancestor (LUCA) retained an obligate endolithic lifestyle. The Bacteria and Archaea–Eukaryota last common ancestors independently evolved cell membranes with the resulting cells colonizing open water. Crossing this environmental threshold greatly enhanced the biomass of the successful organisms and their efficacy in finding new vents. A search for conservative endolithic microbes that lack cell membranes is certainly warranted.

(a) *Duration of hydrothermal chimneys and dispersal*

Life needs to disperse in order to survive. In terms of current threshold theory [23], the nascent life needed to achieve dispersal efficiency where there was a net colonization of new sites, as well as faithful reproduction and resource gathering. Dispersal mechanisms occurred early in the RNA world if life originated in hydrothermal vent environments.

The transient nature of ridge axis 'black smoker' vents compounds the difficulty of their high temperatures as pre-biotic venues. These vents wane and cool as underlying dikes cool on the time-scale of years. All vents eventually expire as seafloor spreading moves them away from the ridge axis hydrologic regime. While near the axis, chimneys are toppled by earthquakes and buried by lava flows on a human time scale.

Koonin & Martin [18] recognized that the nascent hydrothermal chimney organisms envisioned by Lane *et al.* [16] and Russell *et al.* [6] needed to disperse, and that alkaline hydrothermal chimneys are brief but finite duration features on the Earth. Discharge of warm waters from off-spreading axis serpentinite chimney fields, like those observed at Lost City in the Atlantic Ocean, are relatively long-lived with estimates exceeding 30 000 years [24]. Individual chimneys are altered by reaction with ambient sea water [25] and last approximately 1000 years [26]. Continental hydrothermal systems, as on island arcs, rifts and hotspot volcanoes, provide longer duration aquatic niches. Individual chimneys and travertine fields, however, eventually suffer much the same fates as axial marine chimneys. On the other hand, vast numbers of vents, travertine fields and chimneys have coexisted on the Earth at any one time.

Koonin & Martin's [18] nascent life (effectively the porous chimney material) dispersed mechanically as chimneys grew and toppled. Mineral cementation lithifies chimneys above modern serpentinite vents, but the actively growing parts of chimneys are friable (D. Kelley 2010, personal communication). Mechanical dispersal seems feasible for obligate endolithic organisms that lacked cell membranes [16] if large numbers of chimney fields existed. Toppled chimneys produced numerous fragments, many of which

contained organisms. Large gravity driven landslides of unstable chimney edifices launched turbidity currents, which aided physical dispersal. Some of the finest particles were transported in suspension before eventually settling. We note that present day marine currents transfer sand and even pebble-sized material along the seafloor.

(b) *Energy sources*

Chemical potential gradients involving ionic (H^+) or aqueous ($H_{2(aq)}$) hydrogen were important aspects of viable energy sources for early life. Lane *et al.* [16] and Russell *et al.* [6] invoked a pH gradient between 9 and 11 in vent waters and approximately 6 in the ocean as life's first energy source. The thermodynamics are simple; most of the divalent cations in uppermost seafloor basalt entered carbonate, and the ocean was modestly supersaturated with calcite $CaCO_3$. Below $100^\circ C$, ocean chemistry then depended mainly on pCO_2 and only weakly on temperature (see fig. 2 of Morse & Mackenzie [27] for example). At 3 bar pCO_2 , the ocean pH was approximately 5.8; total dissolved CO_2 was over an order of magnitude greater than the present level. Amend & McCollom [1] theoretically predicted a pH 6.5 and 22.7 mM total CO_2 for this situation. Russell *et al.* [6] used pH 5.5. Under pH ~ 6 , comparable masses of CO_2 resided in the ocean and the air. Fe^{2+} was somewhat soluble in weakly acid conditions like in modern anoxic freshwater, with concentrations of approximately 0.12 mM [1]. Aqueous concentration of phosphate was likely approximately 6–9 mM, and along with Fe-phosphate complexes were notably soluble [6]. The solubility of these species is negligible at high pCO_2 if the ocean pH has the modern value of approximately 8.

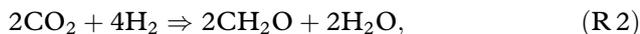
This hydrothermal environment provided ample energy for organisms including LUCA. Aqueous hydrogen ($H_{2(aq)}$), produced during oxidation of ultramafic rocks, reacted with CO_2 from the ambient ocean. In terms of molecular chemistry of extant organisms, these reactions can proceed without adenosine triphosphate (ATP) and hence are likely to be deeply rooted. On the Earth, the presence of abundant basalt and some serpentinite leads to chemical disequilibria when fluids that have interacted with these rock types mix with each other, and with ambient sea water. Basalt, the dominant rock type in ocean crust, has the stronger influence on ocean chemistry, so waters venting from serpentinites into the ocean are to the first-order mixing with waters that reacted with basalt at ridge axes. Amend & McCollom [1] have modelled the thermodynamics and composition of the mixing fluids.

As discussed by Lane *et al.* [16] and Russell *et al.* [6], microbes use H_2 in two generalized ways: (i) methanogenesis, and (ii) acetogenesis. Russell & Hall [5] proposed that this specialization split the domains of cellular organisms: the methanogens evolved into Archaea and the acetogens evolved into Bacteria. Chemically, methanogens reduce CO_2 by H_2 in a dissimilative reaction:



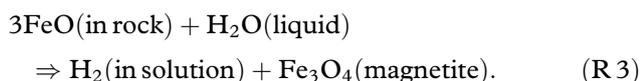
Methanogenic reduction of CO_2 (R 1) provides energy for reactions including the synthesis of ATP from

adenosine diphosphate (ADP) and inorganic phosphate [28–31]. Extant methanogens can inhabit extreme pH environments including high pH ~ 12 serpentinite vents on land [32]. Acetogens reduce CO_2 in an assimilative reaction,



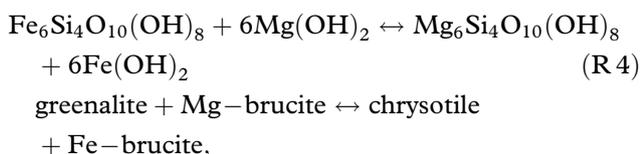
which provides both complex organic matter (idealized formula CH_2O) for the cell as well as energy if the reactants CO_2 and H_2 are abundant (e.g. [33]). The production of acetate ion is favoured over methanogenesis at high pH [5].

Molecular hydrogen required for reactions R 1 and R 2 forms by the oxidation of Fe(II) in rock-forming minerals [34–39]:

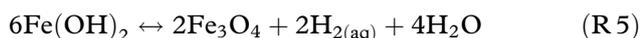


The thermodynamics, however, are complicated because Fe(II) typically occurs as a solid solution in silicate, oxide and hydroxide minerals. Thus, the concentration of the FeO component in the various mineral solid solutions affects the redox state, as does the activity of SiO_2 in the rock and fluid. In particular, hydrogen concentration in the fluid depends strongly on the presence and mode of brucite $(\text{Mg,Fe})(\text{OH})_2$ [40,41] in serpentinite [42]. By mass balance, brucite forms only in serpentine environments where the concentration of SiO_2 is insufficient to include the available divalent cations in serpentine. The stable phases are serpentine plus talc in a somewhat more SiO_2 -rich environment.

We express the serpentine redox reaction as two coupled reactions: the first describes the composition of coexisting Fe–Mg brucite and Fe–Mg serpentine,



where serpentine (greenalite–chryolite) and Fe–Mg brucite are solid-solution minerals. At equilibrium, the Fe : Mg ratio in one solid-solution mineral determines the ratio in the other. Thus, the equilibrium hydrogen concentration can be expressed, for example, in terms of the thermodynamic activity of Fe-brucite component in the solid solution:



Fe–brucite \leftrightarrow magnetite + hydrogen + water.

Reaction (R 5) oxidizes Fe(II) to form magnetite, so the Fe : Mg ratio in product serpentine and brucite (compositionally constrained by equilibrium for reaction R 4) decreases if Mg is conserved in the solid phases and Fe(II) is oxidized (R 5). The equilibrium hydrogen concentration in a flow-through system (expected for natural hydrothermal activity) thus decreases as reactions (R 4) and (R 5) proceed.

Basalt behaves as a silica-rich material where brucite is not stable. Hydrogen is present in fluids vented from basalt but only in small concentrations

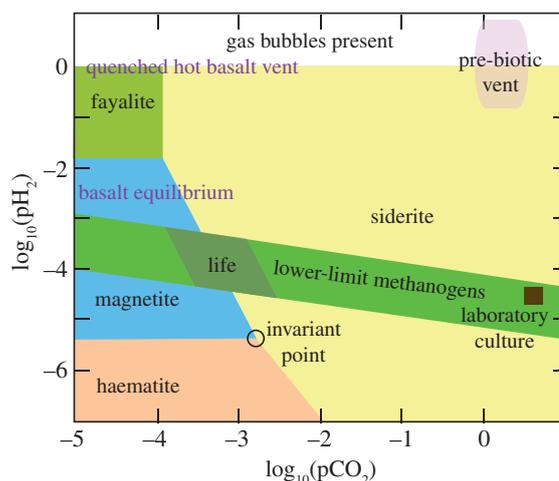


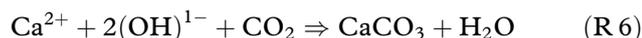
Figure 1. Mineral stability diagram for fayalite Fe_2SiO_4 , magnetite Fe_3O_4 , haematite Fe_2O_3 and siderite FeCO_3 in pCO_2 and pH_2 space in bars at 25°C . The activity of quartz SiO_2 is 1 (saturation). Methanogens can gain useful energy from CO_2 and H_2 above the green line calibrated with the laboratory culture of Kral *et al.* [46]. The approximate pH_2 for black smoker vent fluid from basalt with approximately 1 mMol H_2 is obtained from the field data, laboratory results and thermodynamic calculations. White smokers vents are much more reducing. Fluid equilibrated with basalt at 25°C has $\text{pH}_2 \sim 2.5$ orders of magnitude lower [47]; for reference by stoichiometry, pH_2 in equilibrium with $(\text{Fe}_{0.22}\text{Mg}_{0.78})_2\text{SiO}_4$ (representing basalt) is 1 order of magnitude below that of pure fayalite. Fe(II) is nearly insoluble (from the equilibrium constant product $[\text{Fe}^{++}][\text{pCO}_2]/[\text{H}^+]^2$ at high pCO_2 at $\text{pH} \sim 8$) far to the right of the siderite univariant line ($\text{pCO}_2 > 100$ PAL or 0.03 bar) precluding banded ion formation. The mixing zone of deep marine vents at the time of a clement massive CO_2 atmosphere would have pH_2 and pCO_2 of approximately 1 bar, providing much free energy for methanogens. Modified from [48].

([38,43,44]; see fig. 3 of Sleep & Bird [45] for summary). Black smoker fluids quenched to 25°C have pH_2 of approximately 1 bar and fluids equilibrated at that temperature with basalt still have enough H_2 to marginally support methanogens (figure 1). Methanogens, as a proxy for early life in general, metabolically function at fairly oxidized conditions where disequilibria are possible. The historical tendency to seek extremely reducing pre-biotic conditions should be resisted.

The serpentine–brucite–magnetite redox equilibria depicted by reactions (R 4) and (R 5) proceed spontaneously in response to the influx of H_2 -poor waters into serpentinite. Initial hydration of olivine to serpentine and brucite also proceeds spontaneously, and is strongly exothermic. Both transformations provide potential biological substrates. The low-solubility of total CO_2 in serpentinite fluids, however, greatly limits the productivity of these plausible niches. Carbon isotope studies confirm that life in modern serpentinite systems is carbon limited [49,50].

In addition, the formation of carbonates strongly affects the redox state in serpentine by consuming divalent Mg, Fe and Ca cations into carbonates, which eventually leads to the consumption of the modally less abundant phase, which is commonly brucite. The

activity of di-hydrogen in highly carbonated serpentinite is thus less than that in the starting serpentinite. In more detail, serpentinitization produces $\text{Ca}(\text{OH})_2$ brine from minor amounts of $\text{Ca}(\text{II})$ substituting for $\text{Mg}(\text{II})$ in olivine, as well as $\text{Ca}(\text{II})$ in minor amounts of pyroxene in the rock (i.e. reaction 7 of Reed & Palandri [51]). Calcium does not substitute significantly in serpentine and brucite so it goes into solution that can readily saturate in $\text{Ca}(\text{OH})_2$ at pH of approximately 12. The $\text{Ca}(\text{OH})_2$ -rich water is strongly out of equilibrium with CO_2 in the ambient ocean and the atmosphere; it reacts to form $\text{CaCO}_3(\text{calcite})$. A representative reaction may be expressed in terms of OH^{1-} as



calcium ion(in solution) + hydroxide ion
+ carbon dioxide gas \Rightarrow calcium carbonate (solid)
+ water.

As a consequence of reaction (R 6), natural solutions from serpentinite are quantitatively depleted in CO_2 . The reaction occurs quickly in surface springs with $\text{CaCO}_3(\text{calcite})$ scum plating out like ice on calm water and slush in moving water [52].

In the deep marine setting envisioned by Lane *et al.* [16] and Russell *et al.* [6], calcium carbonate precipitates in the pore networks within the chimney above the vent. Carbonate precipitation depletes Ca^{2+} from the vent fluid; the admixed sea water dilutes Ca^{2+} and increases dissolved total CO_2 to finite concentrations. Mixing, however, reduces the concentration of H_2 and the pH. That is, the mixture has lower CO_2 than sea water and lower H_2 than the vent fluid, reducing the energy available to methanogens (R 1) and acetogens (R 2). With regard to producing ribose from simpler CH_2O compounds [14,15], aqueous CO_2 required to drive abiotic processes is not available at the high pH environment of the pristine vent fluid.

Carbon limitation in serpentine does not necessarily apply on land and shallow marine environments (T. Hoehler 2010, personal communication). The alkaline vent fluid becomes saturated in H_2 at the low total pressure, forming gas bubbles. Sleep *et al.* [38] calculated that the partial pressure of H_2 at the start of serpentinitization is approximately 50 bars at 50°C and 500 bars at 150°C . The bubbles move elsewhere, sometimes into lower pH and more CO_2 -rich fluids including sea water that are controlled by basalt. This process favours origin of life within landmasses. It is also favourable to origin of life on Mars and Ceres where deep oceans were not present and the low gravity caused pressure to increase slowly with depth.

3. WHEN DID LIFE START?

The hypotheses of Lane *et al.* [16] and Russell *et al.* [6] require that the Earth was cool enough (less than approx. 120°C ; [53]) to be habitable, that serpentinite existed on the seafloor, and that the oceanic pH was approximately 6. Below we evaluate these criteria in view of the geological history of the early Earth and the Solar System, noting that the latter constraint on oceanic pH was the most temporally restrictive. We

then address preserved geological evidence for the timing of life's origin, and finally evidence for the existence of serpentinite on the early Earth.

(a) *History of the early Earth*

A brief geological history of the early Earth and the Solar System is necessary to provide a framework for evaluating the evolution of viable ecologic niches. Canfield *et al.* [54], Nisbet & Sleep [55], Nisbet *et al.* [56], Russell & Arndt [4] and Zahnle *et al.* [57] have provided recent reviews. Our treatment closely follows Zahnle *et al.* [58] and Sleep [59]. The Solar System formed within a nebula that became isolated from its parent giant molecular cloud approximately 4.567 Ga (billion years before present). A Venus-sized Proto-Earth collided with a Mars-sized projectile some time before 4.5 Ga. Rock vapourized mainly from the projectile condensed in orbit to form the Moon. Much of the Earth was vapourized, or more strictly heated to a supercritical state where it was vapour at low pressures. The tenuous top (photosphere) of the rock vapour clouds radiated heat to space at approximately 2300 K, cooling the planet to liquid rock in approximately 1000 years. An atmosphere of traditional volatiles, approximately 250 bars of water and approximately 100 bars of CO_2 , remained. (For illustration, we give global masses of volatiles as equivalent pressures in bars; 1 bar is approx. 10^4 kg m^{-2}).

Water clouds condensed at the top of atmosphere. Heat radiated to space at cloud-top temperatures of approximately 250 K. It took approximately 10 Myr for Earth's mantle to freeze and the Moon to move far enough away from the Earth so that gravitational tides were no longer a major heat source [57,58,60]. A solar-heated greenhouse with approximately 100 bars CO_2 above a liquid water ocean at approximately 500 K remained [47,61]. The interior of the Earth was only a few 100 K hotter than present.

Earth's surface could not have cooled to habitable conditions without the eventual sequestration of atmospheric CO_2 as carbonates in rocks. The massive CO_2 atmosphere was out of equilibrium with volcanic rocks on the seafloor, and reaction of CO_2 at partial pressures of well over 1 bar with volcanic rocks occurred very rapidly. This reaction has been suggested as an industrial process to sequester CO_2 [62–64]. However, because the effective thickness of reactable oceanic crust is approximately 0.5 km, carbonation reactions could take up at most approximately 10 bars of the available CO_2 as divalent cation carbonate. The global oceanic crust thus had to recycle at least 10 times into the mantle to sequester the CO_2 -rich atmosphere into Earth's interior. It is unlikely that sequestration was this efficient, as some of the CO_2 -rich crust remelted with contact of the hot mantle, returning the CO_2 to the atmosphere via volcanic processes. Eventually, the mantle cooled enough that subducted crust did not significantly remelt, and the massive CO_2 atmosphere waned. The Earth did not become habitable (cooler than approx. 120°C , [53]) until most of the CO_2 (all but approx. 25 bars) was subducted. The surface was clement (approx. 30°C) only when approximately 1 bar of CO_2 remained.

It was inevitable that Earth's surface passed through conditions favoured by thermophile organisms (approx. 60–120°C) before it became clement. It also had to pass through high-CO₂ partial pressures before it reached the modern condition where a dynamic balance between venting of CO₂ from Earth's interior and sequestration of CO₂ as carbonate in rocks maintains a small but finite atmospheric concentration. However, timing and duration of the demise of the massive CO₂ atmosphere is poorly constrained by theory and the geological record.

The duration of the high-CO₂ clement greenhouse with pH ~ 6 ocean is central to the feasibility of the origin of life within the environmental niche produced in white smoker chimneys. Sleep *et al.* [47] and Zahnle *et al.* [58] did not find any process that would allow this epoch to linger during the early Earth history. Their reasoning is based on the different consequences of internal and surface processes on Earth's CO₂ inventory. Degassing at the ridge axis is an internal CO₂ source that is insensitive to oceanic conditions, while carbonatization of the oceanic crust and its subsequent subduction is a CO₂ sink that involves both external and internal processes. The external (surface) and internal mass balance constraints are coupled by the return of a fraction (F_{arc}) of the subducted CO₂ to surface volcanoes. Formally, the net flux of CO₂ out of the mantle is proportional to the global spreading rate and the subduction rate of seafloor area (A) per unit time (t),

$$\frac{\partial R_{\text{surf}}}{\partial t} = \frac{\partial A}{\partial t} [C_{\text{man}} Y_{\text{ridge}}(T_{\text{man}}) - Y_{\text{carb}}(C_{\text{ocean}}) (1 - F_{\text{arc}}(T_{\text{man}}))], \quad (3.1)$$

where R_{surf} is the mass of the surface, ocean plus air, carbon reservoir on the early Earth, C_{man} is the concentration of CO₂ in the mantle, Y_{ridge} represents the dependence of degassing on mantle temperature T_{man} , Y_{carb} represents the dependence of CO₂ flux into the oceanic crust on total CO₂ concentration in sea water C_{ocean} and the fraction of CO₂ that is subducted deeply depends on the mantle temperature.

Ocean chemistry during the transient clement high pCO₂ atmosphere differed from modern ocean chemistry. Both hot and cool fluids are alkaline at high total sea water CO₂ [65]. Fresh oceanic crust was then a CO₂ and H⁺ sink, not a buffer. Fully carbonatized oceanic crust buffered sea water pH at approximately 6. About half of the surface CO₂ then resided in the atmosphere and half in the ocean. So C_{ocean} in equation (3.1) was proportional to atmospheric pCO₂ and the total surface inventory of CO₂.

A necessary criterion for maintaining this quasi-steady state massive CO₂ clement atmosphere is that the net flux in equation (3.1) was small. The terms in the right-hand bracket in equation (3.1) at that time mainly involved internal processes, so there is no reason to expect that they would sum to a low net flux with only a few per cent of the total CO₂ inventory at the surface. That is, almost all the CO₂ was in the mantle so C_{man} was essentially its maximum possible value. In addition, pCO₂ and C_{ocean} were still high enough that the accessible oceanic crust was fully carbonatized. The factor Y_{carb} was a constant at near its

maximum. As a consequence the mass balance in equation (3.1), once pCO₂ fell well below 1 bar, did involve surface processes. The CO₂ going into the oceanic crust was proportional to total CO₂ concentration in the ocean and this concentration and atmospheric pCO₂ adjusted to provide a buffered quasi-steady state.

Sleep *et al.* [47] and Zahnle *et al.* [58] further quantified the time needed to subduct Earth's initial atmospheric inventory of approximately 100 bars CO₂ by considering a likely range of global spreading rates, or equivalently expressed as a range of lifetimes of the seafloor. Their reasoning followed the common inference that global spreading rates and heat flow were higher in the Hadean than present, and that fully carbonatized oceanic crust carried a global inventory equivalent to 10 bars of CO₂. The briefest predicted time, of approximately 10 Myr for the lifetime of oceanic crust, is based on a value of at least 1 Myr for carbonatization to occur. Their longest sequestration time estimate, 100 Myr, assumed a seafloor lifetime of approximately 10 Myr implies a global heat flow approximately three times the present value. There is enough radioactive and initial heat within the Earth to sustain this heat flux over hundreds of millions of years. This reasoning provides a tentative estimate that the time to sequester the last approximately 25 bars of atmospheric CO₂ was one-fourth of the total time, 2.5–25 Myr. The origin of life under global thermophile conditions (e.g. [66]) remains a viable hypothesis, as does the origin under clement conditions during latter stages of this process.

Herzberg *et al.* [67] discussed the possibility of slow plate tectonics on the early Earth and non-monotonic thermal histories of its interior. It is conceivable, though unlikely because of internal processes that are again involved, that the global spreading rate was quite slow right when the clement high-CO₂ atmosphere existed, giving rise to a protracted quasi-steady state for equation (3.1) or that Earth's interior passed through the right temperature extreme to maintain this steady state as a protracted flux balance. For reference, the lifetime of modern crust is approximately 100 million years, which would suffice to sequester a few bars of CO₂ in tens of millions of years.

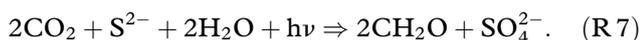
The pH of the ocean evolved during the demise of the massive CO₂ atmosphere from approximately 6 towards the modern state where cations in hydrous silicates within uncarbonatized oceanic crust dynamically buffer the pH of global oceans to approximately 8 [68,69]. High-temperature (more than 250°C) hydrothermal fluids venting from basalt and komatiite are acid, with quench pHs of approximately 3–4, whereas cooler fluids are alkaline. The ratio of hot to cool fluids depends on the hydro-dynamics of sub-seafloor hydrothermal circulation both within and distal to the spreading ridge axis; this is not likely to change much over time as long as seafloor spreading existed. Analysis of the rare earth elements and Y in metamorphosed banded iron formations precipitated from sea water indicates that this buffer was in place at 3.85 Ga in the oldest known rocks that could provide such evidence [70]. Fe(II) is insoluble at pH ~ 8 and high pCO₂, so an open water-banded iron formation is impossible contrary to observations (figure 1).

(b) Record of life on the Earth

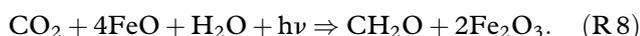
Abundant life appears to have colonized the Earth by approximately 3.8 Ga and to have evolved far beyond the 'RNA world' by this point in the Earth history. Evidence is provided only by the most durable biosignatures that survive extensive metamorphism. We thus follow a functional and least astonishment approach to biology. Cameron *et al.* [71] showed that methanogens fractionate Ni isotopes so there is some hope of finding an ancient durable geological record of this life form. We concentrate on photosynthetic life as its high primary productivity has left a very durable ancient record that has seen extensive study.

Metamorphosed C-rich black shales occur within the oldest known sedimentary sequences in the Isua supracrustal rocks of West Greenland [72,73]. Carbon isotopic values and relative concentrations of U and Th suggest that these rocks are likely a product of anoxygenic photosynthesis [73,74]. This process has been extensively studied in extant organisms. Two pathways allow high productivity that produces a durable geological record.

Some organisms perform photosynthesis by oxidizing dissolved sulphide to sulphate; the idealized reaction is (e.g. [75]),



Other organisms oxidize ferrous iron to ferric iron (e.g. [76,77]),



If buried rapidly, the organic carbon is preserved within low-permeability shales. Conversely, shales consist of mud (clay minerals) weathered from rocks. They are close to thermodynamic equilibrium with their aquatic environments, and thus are a very unpromising substrate for chemoautotrophic organisms and hence non-photosynthetic organic carbon accumulation.

Heterotrophic organisms obtain energy from the reverse of reactions (R 7) [78–80] and (R 8) [81,82]. Microbes capable of obtaining metabolic energy from these reactions inhabit sediments as well as the water column. Pyrite FeS_2 forms when sulphate is reduced in iron-bearing sediments; it occurs in black shales of the Isua supercrustal rocks.

Overall, molecular genomics evidence from Isua indicates that life had already evolved well beyond LUCA at 3.8 Ga [83]. Specifically, bacterial photosynthesis evolved only once and Photosystems I and II in cyanobacteria are related (e.g. [84,85]). Battistuzzi *et al.* [86] and Battistuzzi & Hedges [87,88] proposed that the first photosynthetic microbe is the ancestor of common bacteria clades (Selabacteria, 99% of species). Further, they proposed that Selabacteria soon radiated into Terrabacteria that colonized land and Hydrobacteria that remained in the ocean. Cyanobacteria show molecular evidence of land origin [89]. They are part of Terrabacteria along with the soil microbes Actinobacteria [86–88,90]. We note that the mud (clay minerals) initially forming the Isua black shales suggests that extensive chemical weathering was occurring on land by this period of geological time.

We correlate the Isua supercrustal time-event with the tree of life based on the inference that marine organic carbon in the black shale indicates the presence of photosynthetic Hydrobacteria and the weathering on land indicates a photosynthetic Terrabacterial ecosystem. These inferences do not depend on the detailed placement of Bacteria taxa within Hydrobacteria and Terrabacteria. We do not use molecular clocks to determine times before approximately 3.8 Ga, as we are aware of the pitfalls [91].

Carbon isotopes provide another durable class of evidence for photosynthetic life in the geological record including Isua. Microbial and most plant photosynthetic organisms prefer ^{12}C to ^{13}C . By convention, geochemists express variations in the $^{13}\text{C}/^{12}\text{C}$ ratio in δ notation of parts per mil deviation from a standard, which is a carbonate-bearing marine shell. Hence, marine carbonate deposits have $\delta^{13}\text{C}$ of approximately 0‰. The extent to which $\delta^{13}\text{C}$ of reduced organic carbon is depleted in sediments is variable, with typical values ranging from approximately –20 to –30‰. Mantle-derived carbon from mid-ocean ridge axes has $\delta^{13}\text{C}$ of –5 to –6‰. These ratios are consistent with 15–20% of the carbon from the mantle being ultimately buried as organic carbon and the remaining 80–85% as inorganic carbonate [92].

Carbon isotopic measurements support the antiquity of photosynthesis. Reduced carbon globules/inclusions (2–5 μm) that are widely dispersed in thinly bedded turbidite sediments and sequestered as inclusions in metamorphic garnets at Isua (approx. 3.8 Ga) have negative $\delta^{13}\text{C}$ values [74], as do highly metamorphosed rocks at Akilia (Greenland) at 3.83 Ga [93]. Reduced carbon in sediments throughout geological time shows similar negative $\delta^{13}\text{C}$ values with scatter and secular variations (e.g. [94]). High carbon concentrations and $\delta^{13}\text{C}$ signatures in younger black shales have even survived partial subduction and metamorphism to diamond-bearing gneiss at depths of greater than 100 km [95].

Banded iron formations are also well-preserved geological products of photosynthesis. Organic matter and ferric iron form by reaction (R 8). Although the details of biochemical sedimentation and subsequent diagenesis are not well understood, the Fe- and Si-rich nature of iron formations and the regular bands themselves persist to high grades of metamorphism. Old localities include Isua (Greenland) at approximately 3.8 Ga [72], Nuvvuagittuq (Canada) at 3.75 Ga [96] and Akilia (Greenland) at 3.83 Ga [70,93]. It is possible that banded iron formations formed when ferric iron-rich particles, along with some dead organic matter, sank to the seafloor. That is, the oxidant Fe_2O_3 (and its oxy-hydroxide analogues) was immobile, unlike the modern products of photosynthesis, O_2 and sulphate [97]. Microbes took advantage of the reverse of reaction (R 8) producing haematite Fe_2O_3 , magnetite Fe_3O_4 and siderite FeCO_3 as solids, depending on the bulk composition of the seafloor mixture and the local geochemical environment. Note that the banding formed just below the seafloor and is not true bedding [98]. The ancient ocean lacked SiO_2 -precipitating organisms analogous to modern diatoms so sea water was somewhat supersaturated in SiO_2 . Fe_2O_3 grains sinking through the water

columns catalysed SiO₂ precipitation, so that the material arriving at the seafloor was rich in both SiO₂ and Fe₃O₄. The material segregated into Fe-rich and SiO₂-rich bands during the microbial alteration.

Menneken *et al.* [99] and Nemchin *et al.* [100] reported diamonds and graphite within Hadean zircons, some of which have notably negative $\delta^{13}\text{C}$ values. If substantiated, these results provide a strong bio-signature for photosynthesis, and a record of subduction to at least 100 km depth in the early Earth history. Hopkins *et al.* [101] treated the putative Hadean origin of these diamonds with scepticism in their review, but did not specifically discuss the graphite inclusions. Other laboratories have not found such diamonds despite diligent searches. Neither have other high-pressure minerals been found as Hadean zircon inclusions. Continuing research is warranted.

(c) *Formation of serpentinite*

To fully appreciate the potential of serpentinite as a geo-hydrologic substrate for the origin of life, we first consider this rock type within its geological context, specifically with reference to its petrogenesis and mineralogy. The dominant minerals of serpentinite are serpentine (of various polymorphs, i.e. chrysotile–greenalite [(Mg,Fe)₆Si₄O₁₀(OH)₈]), brucite [(Mg,Fe)(OH)₂] and magnetite [Fe₃O₄], where serpentine and brucite are solid solution minerals with variable amounts of Mg and Fe(II) (crudely with Fe(II)/(Fe(II) + Mg) of approx. 0.1 as in mantle olivine). Serpentinite forms by reaction of olivine-rich [(Mg,Fe)₂SiO₄] rocks with sea water at hydrothermal (less than approx. 350°C) to clement conditions. Solid-state diffusion in olivine is extremely slow below 300°C. Hence olivine is quantitatively consumed at the reaction surface and Mg²⁺, Ca²⁺ and Fe²⁺ do not diffuse back into the olivine crystal, which is necessary for significant magnetite and H₂ production [102].

Olivine is widely present in two geological environments on the modern Earth. It is the dominant component of the upper mantle (from the base of the crust to approx. 400 km depth). The mantle rock peridotite is mostly olivine; it contains lesser amounts of pyroxene, (Mg,Fe)SiO₃ and Ca(Mg,Fe)Si₂O₆, and Al₂O₃-bearing phases including solid solution within Ca-rich pyroxene. These rocks are enriched in Cr, Ni and Co as well as minor elements. Tectonic processes and probably asteroid impacts on the early Earth exposed these types of mantle rocks to surface conditions where they reacted with Earth's fluid envelopes. Modern exposure occurs on land near subduction zones, at fracture zones at mid-oceanic ridges and on seafloor formed at very slow-spreading ridges (less than 20 mm yr⁻¹ full rate). About 10 per cent of the modern deep seafloor has significant amounts of serpentinite [103].

Other olivine-rich rocks form by partial crystallization of magmas within the crust. Moderate partial melting of the mantle generates basaltic magma, the black volcanic rocks of Hawaii, Iceland and the deep ocean floor. Basalt typically has approximately 50 per cent SiO₂, 15 per cent Al₂O₃, 10 per cent each of

CaO, MgO and FeO and minor Na₂O and TiO₂. It is very abundant on the modern Earth; the oceanic crust covering approximately 60 per cent of Earth's surface is mainly basalt and coarse-grained gabbro crystallized from it at depth. Olivine is the first major mineral to crystallize from most basaltic magmas at shallow depths; the cumulate rock dunite formed in this way is mostly olivine.

The interior of the early Earth was hotter than at present, and the MgO-rich lava, called komatiite, erupted under these conditions [104]. There is a geochemical continuum between komatiite and basalt. The main difference for present purposes is that komatiite magmas form more olivine than basalt, and are richer in the minor elements Ni and Co.

(d) *Finding ancient serpentinite*

Serpentinite and its metamorphic products occur in exposures of the approximately 3.8 Ga Isua supercrustal belt of West Greenland (e.g. [72,105]). Hydrogen and oxygen isotope properties of serpentine minerals in these rocks suggest that they are formed by reaction with sea water, as are most extant serpentinites [106]. Chaussidon & Appel [107] showed that the circulating sea water that altered nearby rocks contained significant boron, an element implicated in the formation of ribose [14,15].

There is good evidence that serpentinite was exposed to erosion at least in the early- to mid-Archean. The heavy mineral chromite occurs in both mantle peridotite and cumulate dunite. It is notably resistant to weathering, and is concentrated in heavy mineral fractions of mature sandstones, often co-located with detrital zircons owing to their similar densities [108]. Chromium is mobile during the metamorphism of sandstone to quartzite; it substitutes for Al in muscovite micas, forming the characteristic green mica called fuchsite. Fuchsite-bearing quartzites, some containing relict chromite as cores of authigenic fuchsites, have been identified in the Jack Hills pebble conglomerates of western Australia (detrital ages of 3.1–4.2 Ga; [101,108,109]), the Central Slave Cover Group of the Slave Province (detrital ages of 2.8–3.9 Ga; [110]), the Qianxi Complex from the eastern Hebei Province of China (detrital ages of 3.5–3.7 Ga; [111]), and in the Nuvvuagittuq greenstone belt in the northeastern Superior Province (depositional age more than 3.78 Ga; S. Mojzsis 2010, personal communication). It is reasonable that serpentinite outcropped at Earth's surface at approximately 3.9 Ga.

It is difficult to get direct evidence of still older fuchsites, chromites and serpentinites. There is no good way to directly date putative materials. The low concentration of zirconium and silica in serpentinite prevents zircon from forming there in the first place. Zircons derived from Hadean granites do not preserve evidence of serpentinite; fuchsite inclusions, if present, would be a later contaminant during metamorphism [101].

As a caveat, Bowring & Williams [112] briefly mentioned metamorphosed 'ultramafic rock' in the approximately 4.0 Ga Acasta Gneiss Complex in Canada and subsequent authors have repeated this brief assertion. If correct, this occurrence within a

tectonically active area would indicate that rocks similar to serpentinite outcropped nearby at approximately 4.0 Ga. However, the age of these ultramafic rocks remains controversial, as continued mapping indicates that the ultramafic rocks near Acasta are in fact younger and not relevant to Hadean landmasses ([113]; W. Bleeker 2010, personal communication).

Unlike the Earth, the very early surface geological record is preserved on Ceres and Mars. Carbonate, serpentine and brucite are remotely sensed components of the surface of Ceres [114]. An opaque mineral, probably magnetite, is present. Serpentine has been remotely detected on Mars [115]. It is an uncommon but widespread rock type as on the Earth. It is associated with carbonate, but not brucite. Ehlmann *et al.* [115] note that surface brucite probably reacted with Martian atmospheric CO₂ to form carbonate over periods of geological time where liquid water was present. Brucite may well persist within the underlying rocks. Magnetite is not detectable by the remote methods used to find serpentine on Mars [115].

(e) *Mantle paleontology*

Earth's mantle was not isolated to the geochemical consequences of life's metabolic innovations, specifically, the advent of harvesting solar energy into Earth's geochemical cycles via photosynthesis [116]. We know that surface material subducted into the mantle as sequestration of CO₂ by this process was necessary for the Hadean Earth to cool from the *hellish* conditions for which this eon was named. The carbon-rich subducted domains persist in Earth's mantle and are the source regions for CO₂-rich kimberlites and carbonatites. The oldest evidence of CO₂ subduction comes from alkaline magmas intruded in India at approximately 1.48 Ga [117]. Analysis of the daughter product ¹⁴²Nd of the short-lived (half life 0.103 Ga) isotope ¹⁴⁶Sm in whole rock samples indicates an age of approximately 4.2 Ga, which we associate with subducted oceanic crust. The material circulated through the mantle, melted and intruded the Indian lithosphere at approximately 3.6 Ga (from ²⁰⁷Pb/²⁰⁴Pb and age of surrounding craton). It remelted and ascended to the surface at approximately 1.48 Ga. There is no reported carbon isotopic data on these rocks that would bear on whether photosynthesis occurred at the time of subduction. Archaean CO₂-rich magmas that might have tapped Hadean subducted material also exist [118]. The oldest known one is the approximately 3.0 Ga Tupertalik complex in Greenland [119].

Evidence of subducted photosynthetic material from Archaean and later times are preserved in kimberlites and their diamonds, so there is hope of finding a Hadean record. The occurrence of negative $\delta^{13}\text{C}$ in diamonds ultimately derived from subducted organic carbon is well known [120,121]. Conversely, one seeks evidence for niches of locally oxidized environments owing to concentrations of photosynthetic life, for example, mobilization of U into subducted sediments and not Th as described by Rosing & Frei [73]. As with diamonds, there is post-Hadean mantle evidence of this process. Zartman & Richardson [122] studied

U/Th fractionation in kimberlites, noting that at 2.7 Ga they had a bulk Earth U/Th value. After the advent of extensive oxygenic photosynthesis, the ratio increased over time to twice the bulk earth value as dioxygen concentration increased in the atmosphere.

There are even subtle photosynthetic effects on mantle rock. Moissanite SiC along with Fe–Si metal compounds, and native Si, occurs as rare components of mantle-derived rocks, including chromite-rich exhumed mantle and kimberlites (e.g. [123]). Fang *et al.* [124] described qusongite (WC) and other strongly reduced minerals from chromite-rich mantle. SiC has strongly negative $\delta^{13}\text{C}$, indicating the distinct possibility of subducted organic matter [123].

4. CONCLUSIONS

Geological observations suggest that the Earth teemed with life by approximately 3.8 Ga, with substantial geochemical evidence of photosynthesis being preserved in ocean floor sedimentary rocks. Evidence for life before this time is meagre. The geological record of life in Earth's mantle is largely unexploited. That is, mantle palaeontology may contain the only biogeochemical evidence of life prior to approximately 4 Ga. Geologists can currently say that the Earth cooled from an initially hot state sometime after 4.5 Ga, and over the first approximately 0.5 Ga evolved into environmental conditions favourable for the dawn of life. Geologically, we know very little about the timing or the duration of the 'RNA world'.

Submarine hot springs above serpentinite produced mineralized deposits (chimneys) that are very attractive pre-biotic venues: an environment that provided geochemical free energy, reactive mineral surfaces and protective pore spaces in rocks to concentrate life's 'building blocks', as well as template and catalyst mineral species. Lane *et al.* [16] and Russell *et al.* [6] argued that this is a far more favourable environmental niche than the primordial soup in Darwin's pond. Mathematical modelling indicates that '*autocatalytic soup*' does not evolve ever-increasing complexity, but repeatedly returns to certain states [125].

The nascent life in the hypotheses of Lane *et al.* [16] and Russell *et al.* [6] used a pH gradient between vent fluid of 9–11 and ocean water with pH ~ 6. Carbon was not limiting with pCO₂ of approximately 1 bar. Fe(II) and P were reasonably soluble, in contrast to modern times where carbon is limited owing to low pCO₂, oceanic pH ~ 8, and Fe(II) is insoluble. This reasoning provides a narrow window of several million years for the origin of life when the last of Earth's massive CO₂ atmosphere was subducted into the mantle. The pH ~ 6 ocean cooled through both thermophile and clement conditions. Life's origin in either is viable. The geological record is currently *silent* on these alternatives, and on their timing and duration. At present, we lack geological evidence of oceanic pH before the advent of photosynthesis.

We see no direct evidence of serpentinite at the *dawn of life* because rocks that might contain this record have not been found. We do see evidence for serpentinite back to approximately 3.9 Ga. Modern vents provide a good analogy to the pre-biotic Earth as sea water

reaction with mantle-derived rock dominates vent fluid chemistry. There are subtle differences in that there was no free oxygen and much less sulphate in the open ocean water entering the hydrothermal systems. The sulphide concentration in vent fluids was approximately one-half that of present [126].

Finally and perhaps ironically, the hypothesis that life originated on Mars or Ceres and then came to the Earth on ejected rocks is more testable than terrestrial origin. These inactive bodies sequester very ancient rocks. They are just logistically difficult to sample.

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