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# The inevitable journey to being

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Life is evolutionarily the most complex of the emergent symmetry-breaking, macroscopically organized dynamic structures in the Universe. Members of this cascading series of disequilibria-converting systems, or engines in Cottrell's terminology, become ever more complicated—more chemical and less physical—as each engine extracts, exploits and generates ever lower grades of energy and resources in the service of entropy generation. Each one of these engines emerges spontaneously from order created by a particular mother engine or engines, as the disequilibrated potential daughter is driven beyond a critical point. Exothermic serpentinization of ocean crust is life's mother engine. It drives alkaline hydrothermal convection and thereby the spontaneous production of precipitated submarine hydrothermal mounds. Here, the two chemical disequilibria directly causative in the emergence of life spontaneously arose across the mineral precipitate membranes separating the acidulous, nitrate-bearing CO<sub>2</sub>-rich, Hadean sea from the alkaline and CH<sub>4</sub>/H<sub>2</sub>-rich serpentinization-generated effluents. Essential redox gradients—involving hydrothermal CH<sub>4</sub> and H<sub>2</sub> as electron donors, CO<sub>2</sub> and nitrate, nitrite, and ferric iron from the ambient ocean as acceptors—were imposed which functioned as the original 'carbon-fixing engine'. At the same time, a post-critical-point (milli)voltage pH potential (proton concentration gradient) drove the condensation of orthophosphate to produce a high energy currency: 'the pyrophosphatase engine'.

The general struggle for existence of animate beings is therefore not a struggle for raw materials—these, for organisms, are air, water and soil, all abundantly available—for energy which exists in plenty in any body in the form of heat . . . , but a struggle for entropy . . . . . [1]

## 1. The self-organizing universe

Given the extraordinary success of molecular genetics these days, it seems bad form, not to say ignorant, to consider the emergence of life in terms other than of the RNA world. However, the obvious need to drive inherently endergonic chemical processes and sustain far from equilibrium states, not least to get a metabolizing system going to manufacture the nucleotides in the first place, casts doubt on such molecular vitalism. Of course, encouraged by the myriad of abiotic molecules dispersed throughout space and brought to the Earth as dust and in carbonaceous chondrites or generated through lightning, one might consider instead spontaneous generation from a prebiotic organic world. However, then, one would have to (i) overcome the infamous dilution problem, (ii) deal with the fact that the early atmosphere was relatively oxidized, (iii) explain how the inept earliest cells gained their energy, nutrition and catalysts and how chemiosmosis got started, and (iv) deny the plain force of Schrödinger's 1944 stricture regarding 'an organism's astonishing gift . . . of "drinking orderliness" from a suitable environment' [2–4]. Indeed, the apparent reluctance to dismiss the simple idea of the organic soup as the recipe for the origin of biochemistry puts one in mind of how spontaneous creation held back the field of cell biology in the two centuries between van Leeuwenhoek and Pasteur [5]. Instead, an overarching theory for life's emergence is clearly required, one which first of all

takes properly into account the thermodynamic requirements inherent in the so-called order-creating processes, those mediating the first steps in the emergence of life in particular, and second takes appropriate advantage of the torrent of new pertinent information pouring out of both the life, and the earth sciences.

To this end, we first place the emergence of life in its full context of the order-creating processes operating in the Universe. Our point of departure is this remark taken from Kondepudi & Prigogine [6, p. 427]: ‘One of the most profound lessons of nonequilibrium thermodynamics is the dual role of irreversible processes: as destroyers of order near equilibrium and as creators of order far from equilibrium’. And we begin by noting two key points about this observation. First, for an irreversible process to be maintained within a system, it must be embedded in, and exchange energy and/or material with, a larger system that is itself in disequilibrium, i.e. itself is ordered. Further, the embedding must be such that the overall system frustrates to some extent the flows acting to dissipate that embedding disequilibrium. Therefore, an externally imposed order, one whose dissipation is significantly frustrated, is needed to drive a system into disequilibrium, and potentially far enough from equilibrium that order-creating irreversible processes will arise within it. In other words, it takes (the dissipation of) order to create order. Second, the order that arises in this way is always an engine—an engine that acts to accelerate the dissipation of the disequilibrium that drove it into existence in the first place and upon which it feeds [7]. As such it is driven by a greater entropy-producing flow that is dissipating the embedding disequilibrium and producing work in the form of a lesser entropy-consuming, i.e. order-creating, flow. Engines are thus disequilibrium converters, or in more conventional terms, free energy converters. Furthermore, and critically, such engines are always autocatalytic, either directly or indirectly; made so by the fact that the work they produce acts back on the engine with the effect of increasing its throughput and stabilizing it against decay [8]. It is because of this positive feedback that the engines are emergent, and self-organizing, and it is through the resultant autocatalytic growth, that they accelerate the rate at which the driving disequilibrium is dissipated. Thus, there is the paradoxical fact that far-from-equilibrium order, in its haste to be dissipated, is compelled to create order—in the form of engines of dissipation—that it might accelerate its dissipation. All order in our present universe is presumably born of this paradox. Order, therefore, is inherently dynamic, transient and hierarchical and—in obedience to the second-law’s diktat that all change must increase the entropy of the universe—serves to quicken that increase through the concomitant destruction of order by the transient creation of order.

Indeed, this has been the business of our Universe since its birthing in the Big Bang—the initial condition—at which moment it stood at an almost unimaginable distance from equilibrium, and thus in a state of nearly infinite thermodynamic stress [9–12]. Its evolution since has been solely about dissipating that disequilibrium at the maximum achievable rate. This it has done, and is doing, largely by creating order in the form of engines of dissipation—of emergent, self-organizing, autocatalytic engines, as we noted earlier, whose thermodynamic *raison d’être* is to open and/or widen the channels of dissipation that mediate the relaxation of the particular disequilibrium that

gave each its birth and upon which it feeds [7]. However, each such engine does only a small part of the total job and each itself is, and creates, a new disequilibrium—a new ordered state—which, in turn, induces the creation of subordinate engines to devour and dissipate it, as we noted earlier. The vast industry of cascading dissipation-accelerating engines that emerge in this circumstance forms a great, evolving, self-organizing, dynamic web.

Our particular concern here is to demonstrate how life is a natural and expected outcome of thermodynamically driven order creation through symmetry-breaking in our far-from-equilibrium Universe. To this end, it is helpful to have a clear understanding of what is required to give birth to a dissipative engine, and as part of that what controls the transition between order-destroying and order-creating dissipative processes as referred to in the earlier-mentioned quote from Kondepudi & Prigogine [6]. For this, we need to delve a bit into the theory of non-equilibrium thermodynamics and open systems—a theory largely initiated by Onsager [13] who analysed the near-equilibrium realm, but which received its original general development at the hands of several investigators, including De Groot & Mazur [14], Jou *et al.* [15] and Prigogine [16] (together with his co-investigators; principally Glandsdorff & Nicolis [17,18]).

Such systems, Prigogine first argued, go through qualitatively distinct phases as a function of how far from equilibrium they are driven. In the near-equilibrium region, which Prigogine called the thermodynamic branch [16–18], the thermodynamic forces induced by the free energy influx give rise to fluxes which (i) are proportional to the forces and, most importantly, (ii) respect the symmetries that characterize the system at equilibrium. That is, the dissipative fluxes induced in this branch do not involve macroscopic organization, and thus have the same high spatial and temporal symmetry of the equilibrium state. Furthermore, the flows induced in this realm are stable dynamic states in that the system responds to perturbative fluctuations by damping them out exponentially. Thermal conduction is an example. As the system is driven further from equilibrium by increasing the strength of the free energy influx, a critical point is reached (the bifurcation point) at which this equilibrium-like dynamical behaviour is no longer stable, and the system responds to perturbing fluctuations by diverging into a new state which is (i) stable to perturbations in the post-bifurcation region, (ii) does not honour all of the symmetries of the equilibrium state (i.e. symmetry breaking), and (iii) is symmetry breaking because it involves flows and structures that are macroscopically organized; that is they have structure at the macroscopic scale—convection cells being the graphic example as we shall investigate in §4. Such organized dynamic states are called dissipative structures by Prigogine and are inherently low entropy and are therefore, inherently unstable and transient forms of matter.

It is important to note that these self-organizing dissipative structures are free-energy-converting (FEC) mechanisms; as noted earlier, they tie together a free-energy-consuming flow and a free-energy-generating one—as the engine’s work output—into a single, indivisible and spontaneous thermodynamic process. Cottrell [7] has aptly identified these structures as engines. However, as was also noted earlier, they are in addition quite phenomenal engines in being, either directly or indirectly, autocatalytic (not only do they corral the energetic and material output from a preceding

engine, but also consume the disequilibrium free energy they produce as engines to maintain and grow themselves). And we may take Cottrell's exegesis on Prigogine's argument [7] to further imply that all macroscopically organized non-equilibrium arrangements of matter and energy owe their existence to the kind of far-from-equilibrium self-organizing, FEC engines described by him.

However, to this general picture, Cottrell has added an important qualification—namely that not all naturally arising FEC engines need generate from scratch and by themselves their own broken symmetry-organized structures that can operate as their coupling device. In some cases, the structures are already present—at least in a form sufficient to seed, or template the autocatalytic growth of a new engine—and are present as the by-product of the operation of independent and in general unrelated dissipative engines. In these cases, driving gradients of relatively modest strength can be sufficient to initiate dissipative engines and keep them fed and growing. An example of this as it applies to the emergence of life are the *inorganic* prebiotic mineral structures involving iron sulfides, dosed with nickel, cobalt and molybdenum and the iron oxyhydroxides, so similar to the active centres of the metalloenzymes, that played a vital role in the first metabolic pathways [19–21].

Therefore, in our search for the FEC engines that would have been required to energize the emergence of life, we need to keep in mind both ways in which such engines can arise. And it is clear that in broad strokes, the dissipation hierarchy taking us from geological dissipation to life is very likely to have been a mix of both types—and possibly indeed of hybrid types. Furthermore, embedded in this dissipation typology is the profoundly important distinction between—and transition between—primarily physical and primarily chemical dissipative engines. It is clear that various types of engines, drawn from this palette of options and driven in series, are involved, and culminate in, life's emergence: in the terminal steps in the cascade set in motion by the Big Bang; these include gravitational accretion, tectonic convection, serpentinization and the chemical free energy conversions of proto-metabolism to hit just a few high points [22–27]. Although the primary engines in this hierarchy are essentially large and physical, i.e. solar system and planetary accretion and then whole body thermal convection in the mantle; downstream the engines are hybrids, involving ever more chemical and eventually electrochemical energies, whereas the newly emergent physical mechanisms are nanometric. It is the coupling of serpentinization, through hydrothermal convection, to the formation of porous submarine mounds that is of most concern here. Indeed, it is the serpentinization of peridotite—the magnesium iron silicate comprising portions of the floor of both the first ocean and parts of the ocean today—that offers us still an observational gallery to the operations of life's parental engine. We turn next to connecting the self-organizing dynamics of the Universe as they act at the astrophysical scale to those which produced the engines leading directly to life.

## 2. From astrophysical to terrestrial engines of dissipation

It is ultimately the dynamics of the geometry of space–time itself, which is to say the force of gravity, that has driven the self-organization of the Universe which is everywhere

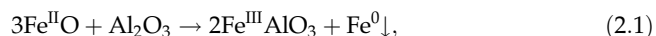
in the form of engines accelerating the dissipation of order. That is, this great drama too is thermodynamic in nature and its ultimate driver is the tendency of the curvature of space–time, in the presence of distributions of mass, to increase locally, and grow more complex, more entropic, with time [12].

As this implies, gravitational collapse is, counterintuitively, a second-law-abiding, entropy-producing process, one whose limit (albeit a transient one—if trillions of years counts for transiency [11]) is the black hole state in which the entropy per unit mass (and the curvature of space–time) is maximal [22]. Importantly, however, reaching that maximum is a remote and frustrated—and potentially even futile—dream for much of the mass of the Universe. Impeding the way are a variety of obstacles [28, ch. 4]. Two have particular relevance to the emergence of life. First, the conservation of angular momentum obliges all gravitational collapse not proceeding from a state of near-perfect spherical symmetry to go no farther, initially, than into the formation of vast spinning vortices; vortices that fragment into hierarchies of lesser vortices. At this hierarchy's top stand giant assemblies of galactic clusters, each cluster containing immense inventories of galaxies, each of these with immense inventories of stars (not to mention many other forms of matter and energy). All these dynamic structures too are engines of dissipation, albeit engines that grind exceedingly fine. Second, there is the obstacle of nuclear fusion, which postpones further collapse of star-sized clumps, while providing the FEC engines of greatest direct relevance to the existence of life, until, that is, the hydrogen endowment of each has been consumed and its fire dies. Providentially, of course, more massive stars are shorter lived, and in their necessarily unpeaceful deaths bequeath to their cosmic neighbourhoods all nuclei beyond lithium—and thereby make it possible for subsequently formed stars to host wet, rocky planets; rocky planets most vitally with a healthy endowment of radionuclides bearing billion-year half-lives—sufficient, that is, to keep a rocky planet of good size in a tectonic boil—at least for the time required for the fledgling of life to take wing on the updrafts from serpentinization, taking advantage as it does of those other trans-lithium elements for catalysis all the way up to atomic number 74, tungsten [20]. In any case, it is in the accretion of rocky planets that the Universe's cascade of engines finally descends to the point where the order produced directly sets the table for the emergence of life [29]. But how that table is set depends on just how the accretion process takes place.

In detail, planetary accretion proceeds through runaway growth of ever larger wet rocky bodies comprising magnesium silicates and nickel iron bodies, comets and carbonaceous chondrites, though collisional erosion is also involved [30–32]. Once the rocky bodies have the dimensions approaching our Moon, such planetesimals collide to produce the terrestrial planets [32]. Primeval gases still surrounding these proximal planets are blown outward by solar winds beyond the so-called snow-line to the colder reaches of the system [33–35]. The chemical and mineralogical composition of rocky bodies depends on the make-up of the protoplanetary disc. For example, those with a carbon:oxygen ratio twice that of our Solar System would produce dry and lifeless silicon carbide planets [36,37]. In our own system, carbonaceous chondrites merely added to the carbon budget of the wet siliceous rocky planets and the moons of Jupiter and Saturn, born as it was of multiple supernova explosions [11,38]. The chemical composition of the

gases that remained dissolved in our own planet's hot interior was controlled by its mineralogical composition—in particular of iron [3].

Once the Earth reached a critical size, gravitational and radiogenic heat melted the heterogeneous mantle accreted from dense native iron and less dense silicates. The larger iron bodies would have sunk towards the centre of our spinning world, dissolving dense blobs as they did so, picking up speed and dragging more in their wakes, generating even more heat until landing in, and as, the core. The remaining ferrous iron then self-oxidized to the smaller ferric iron under these high pressures and partitioned into the aluminous silicate perovskite fraction (approx.  $\text{Al}_2\text{O}_3$ ), the dominant mineral in the lower mantle [39,40]:



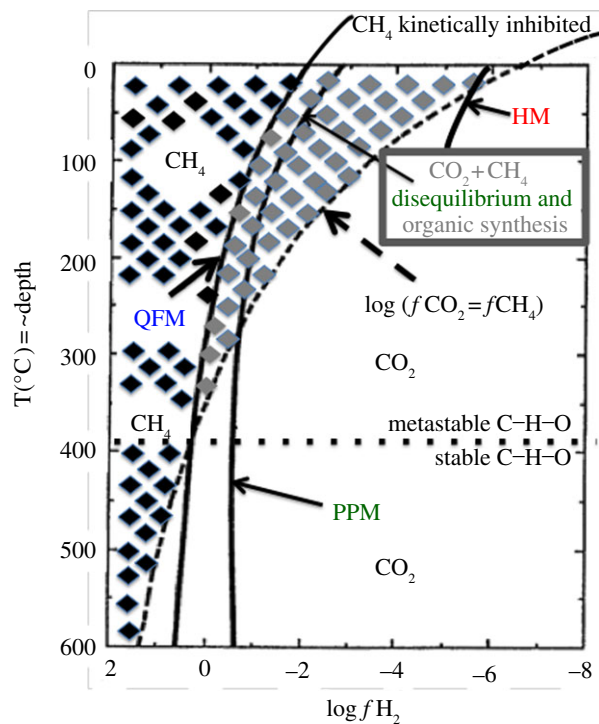
while the native iron fraction left over joined the gravitational scramble to the core. This reaction left the mantle with a surprisingly low hydrogen fugacity (i.e. a relatively high oxygen fugacity) such that the state of carbon dissolved or present in the mantle was as its oxide (figure 1) [41].

Thus, the fate of carbon in the early Earth was to be oxidized to carbonate or carbon dioxide within the first 100 Myr [42]. The upshot was that volcanoes dispensed great volumes of  $\text{CO}_2$  to the early atmosphere as Darwin [47], Haeckel [48], Mereschkowsky [49] and Leduc [50] had surmised. Indeed, a pressure of 10 bar or more was likely at least at times when carbonated ocean floor was reheated in mantle down-draughts and the gas returned to the atmosphere [42,43]. Hydrogen too was essentially oxidized at these high temperatures to water vapour, and it too was exhaled to produce the all-enveloping universal carbonic ocean perhaps 8 km or so deep [51,52]. Other oxidized volatiles were pyrophosphate, nitric oxide and sulfur dioxide [53–56].

### 3. Driving for life: convective engines

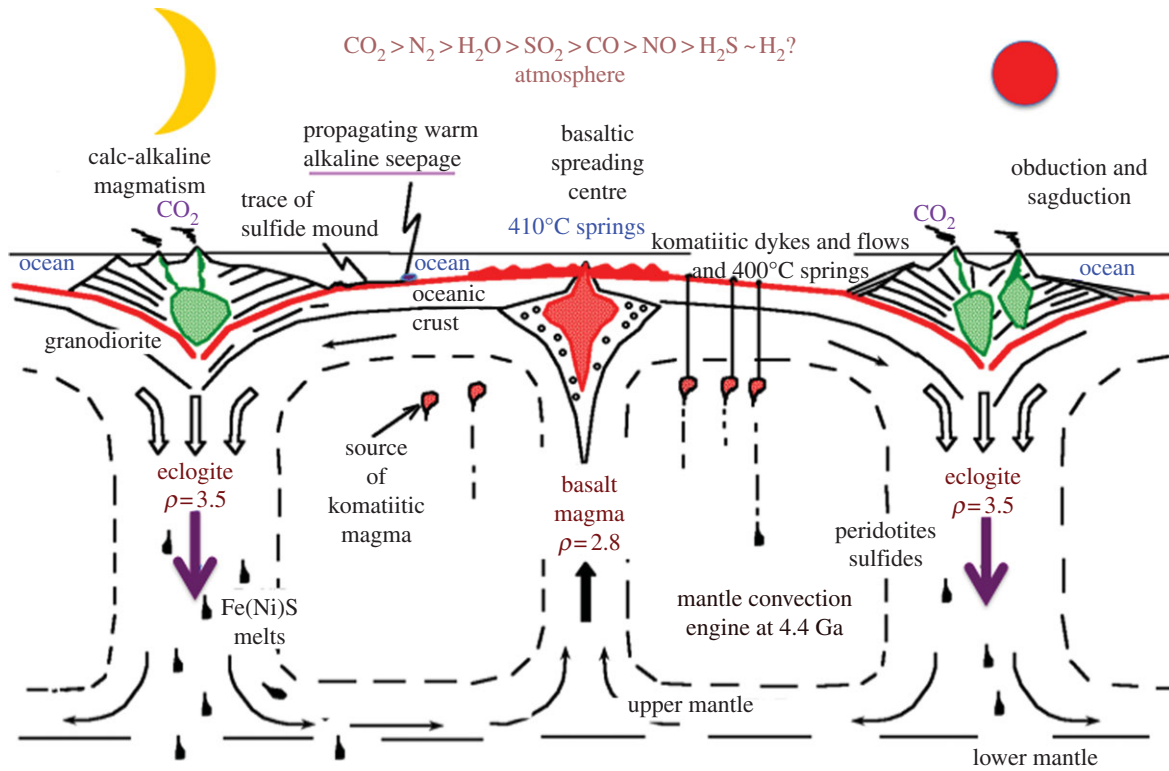
The gravitational and radiogenic heating of the Earth's rocks generated a gravitationally orientated thermal gradient that exceeded the Rayleigh limit and therefore (as prescribed by Prigogine) gave rise within the mantle to organized, autocatalytic convective engines of dissipation. It is, of course, to these engines that we ultimately owe the creative, far-from-equilibrium tectonic dynamism of our planet. In turn, these convective flows both drove and were accelerated by another self-organizing dynamics to which they were coupled, namely density-dependent chemical fractionation—fractionation between relatively buoyant magnesium-silicate-rich minerals that became enriched in the upper mantle, and denser, native iron masses and globules preferentially relegated to the core. The resulting, continuously refreshed, mineralogical organization of the planet, whose mechanistic details we review next, was no less essential to its ability to spawn life.

As gravitational energy drove the differentiation of the iron core, conversely the relatively buoyant, magnesium-silicate-rich upper mantle began to rise differentially upward. Whether in the Hadean, these mass transfer convective flows were in well-organized convection cells as they are now and thereby drove conventional plate tectonic activity or were less organized and mainly involved mantle plumes is much disputed [27,57]. Whichever the dominant form, it was inevitable that ocean floor would have been



**Figure 1.** The oxidation state of the upper mantle 100 Myr after its formation was controlled by the quartz/magnetite/fayalite buffer (QFM =  $\text{SiO}_2/\text{Fe}^{\text{II}}\text{SiO}_4/\text{Fe}^{\text{II}}\text{Fe}_2\text{O}_4$ ) [3,40,42]. The dominant state of carbon in the upper mantle was as its full oxide with vanishingly small concentrations of methane (black diamonds) [41], explaining why the early atmosphere, mainly supplied by volcanoes, was dominated by  $\text{CO}_2$  along with nitrogen and lesser  $\text{SO}_2$  and  $\text{NO}$ . However, as shown by Shock [43], there is a cross-over of the oxidation states of carbon and iron very approximately at around  $400^\circ\text{C}$ . At the lower temperatures towards and at the surface of our planet the equilibrium state is methane (grey diamonds) as produced in hydrothermal systems through serpentinization [44,45], though the abiotic reduction of  $\text{CO}_2$  at the Earth's surface is thermodynamically challenged. It is this metastable field (grey diamonds) that Shock [43] termed 'the locus of biochemistry within geochemistry'. However, iron minerals comprising the QFM buffer would also tend to catalyse the reduction/hydrogenation of  $\text{CO}_2$  to formate and methane. A further buffer (PPM = pyrite/pyrrhotite/magnetite or  $\text{Fe}^{\text{II}}\text{S}_2/\text{Fe}^{\text{I}}\text{S}/\text{Fe}^{\text{II}}\text{Fe}_2\text{O}_4$ ) operating where sulfide is concentrated would also tend to control the oxidation state of carbon at lower hydrogen fugacities and might be expected to catalyse redox reactions. The even more oxidized HM buffer (haematite/magnetite or  $\text{Fe}_2^{\text{III}}\text{O}_3/\text{Fe}^{\text{II}}\text{Fe}_2\text{O}_4$ ) would be comparable to the mixed valence mineral green rust (e.g.  $[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{OH})_4]^+[\text{OH}]^-$ ) which might oxidize methane to organic intermediates at temperatures around  $40^\circ\text{C}$  [46]. Note how the redox state of iron contributes to the geochemical conditions that drove life into being and thereafter was central to its further evolution. Based on Shock [43].

continually renewed. Holmes [58] was first to provide a viable mechanism for the formation of new ocean floor formation as an aspect of thermal convection of the Earth's mantle not restricted merely to reliance on buoyant mantle updraughts. His mechanism involved a catalytic feedback caused by a mineralogical phase change, one induced by pressure so that the density of the now cool, down-welling limb continuously increased, pulling the advecting ocean floor behind it, so acting in concert with the push from the rising limb. The phase change involved olivine, pyroxene and feldspar, with a density of approximately  $3.0 \text{ kg dm}^{-3}$ , that metamorphosed to eclogite (a garnet pyroxene rock) with a density of approximately  $3.5 \text{ kg dm}^{-3}$ , so providing



**Figure 2.** Diagram to show how a mantle convection engine continually provided new and reactive ocean floor in the Hadean as well as oxidized volatiles to feed the hydrosphere and atmosphere [24,27]. Hot buoyant updraughts of partially molten mantle transfer heat to the surface, so dividing and pushing the ocean floor apart. At the same time, a density inversion drives the basalt-to-eclogite transition which, in turn, produced further gravitational energy to the downward-pulling limbs with friction regulating flow rate [58]. Thick ocean lava plateaus were another result of mass transfer of heat in mantle plumes towards the Earth's surface. The atmosphere was relatively oxidized though the proportions of its components are not well constrained [3,42,52,55]. The figure provides a framework in which to understand the chemical and thermal energies produced in such an environment from submarine water–rock interactions that drove anaerobic litho-chemosynthetic life into being in a submarine hatchery around 4.4 Ga. It took more than another billion and a half years for wide littoral continental areas to develop and provide a nursery for burgeoning oxygenic photosynthesizers around 2.7 Ga [25,61–63]. Adapted from Russell *et al.* [24].

the body force to help drive this engine. Such a process might be expected to have operated with even more vigour in the Hadean when the oceanic crust was richer in olivine and the temperature of the mantle was perhaps 200°C hotter than it is today [59,60].

We have adopted a similar ocean floor spreading mechanism to explain the continual renewal of ocean floor in the Hadean driven by just the catalytic feedback mechanism envisaged by Holmes but with the added contribution of magmatic plumes rising vertically from the core mantle boundary [27,30,57,58] (figure 2). Bédard [64] has suggested that such vertical tectonics would also involve the transition to dense eclogite in a catalytic mechanism involving delamination of the lower crust whereby the descending eclogite would guide repeated updraughts of mantle material while at the same time augmenting the differentiation of silicate magmas to produce high temperature submarine hydrothermal exhalations (cf. [65]). These exhalations would help provide the trace elements to the ocean required of life's inorganic catalysts as described in §§4 and 5 [25,61].

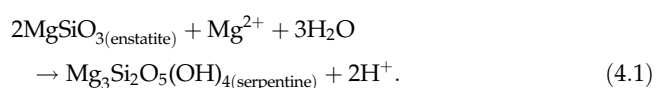
#### 4. Serpentinization: life's mother engine

One effect of mantle convection is to stress the new and relatively homogeneous oceanic crust beyond its elastic limit, i.e. its brittle strength. Stresses may be tensional and/or compressional. Given the irregular textures of the magnesium + iron + (alumina)-silicate lavas such as komatiite and basalt,

and magmatic intrusions such as peridotite or gabbro comprising the early ocean floor, any resulting fractures that penetrate the surface will tend to be somewhat irregular, thus increasing permeability and allowing access to ocean water which then gravitates to depth. Again, a positive feedback is realized in that the hydrostatic pore pressure increases the effective stress such that the fractures tend to extend. Fracturing loads the next weakness which then fractures in turn. Or rupturing is prevented by a mineral knot and stress accumulates which has to find a new weak zone of fracture [66]. Hydration locally increases rock volume, causing secondary stresses and strains. Thus, populations of reproducing parallel, tensional or sheer and interleaving cracks and fractures propagate as do secondary and tertiary fractures as the stresses are modulated by newly formed free surfaces. Elastic and chemical energies stored in crystals at the fracture tips are transformed into surface free energy which, in turn, is stored at the crystal surface at the breaking point of imminent ductile to brittle rupture/failure during hydrofracturing [66–68]. This stored chemical energy may be used to reduce the percolating water and carbon dioxide to hydrogen, formate and methane as explained below [44]. In such a stressed system, the longer the fractures, the less the energy required for their further extension and reproduction, i.e. they are autocatalytic [7]. The failure points absorbing, i.e. they are autocatalytic [7]. The failure points absorbing and converting the tectonic free energies are, moreover, engines that can produce more engines [7]. Submarine hydrothermal convection cells that serpentinize the crust in this fashion and transfer heat to the ocean are of two main

types: (i) a hot (400°C and above) magma-driven system over spreading centres and magmatic plumes and (ii) open system non-magmatic convection cells (less than or equal to 150°C) operating in the older, cooling crust away from such centres (figure 2).

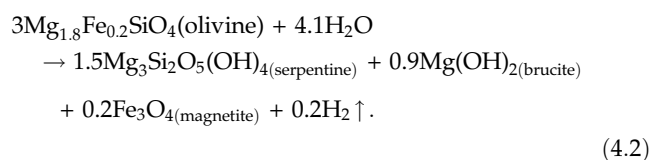
The first type of aqueous submarine convection cell, the 400°C and above cell forced by magmatic intrusion emerging from the mantle convection engine or at magmatic plumes, played merely the supporting role in the emergence of life of loading the Hadean Ocean with catalytically potent transition metals. The intrusion of magma caused tensional rifting, especially at ocean spreading centres. Water gravitated down these active rift faults until the pressure-dependent buoyancy of magnesium-bearing salt water at its critical point at around 410°C drove the fluids back to the surface. At the critical temperature these fluids were, and are, buffered to acidic pH as magnesium silicate hydroxides are formed from the pyroxene enstatite, with the generation of high temperature serpentinite and the release of protons (figure 2) [61,69] (equation 4.1):



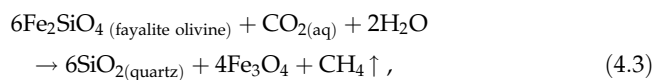
These acidic waters dissolved the transition metals (iron, nickel, zinc, cobalt and tungsten) from the oceanic crust and dispensed them to the carbonic Hadean Ocean where they remained in often supersaturated solution until they met submarine alkaline, moderate temperature springs. Thus, the Hadean Ocean acted as an effective reserve for metal catalysts for emergent life, and eventually for the active centres in peptides and proteins [70–76]. We recognize these high temperature systems today as the iconic black smokers—black because unlike in the Hadean, the metals precipitate rapidly on meeting alkaline oxidized ocean waters [77,78].

It is the second, lower temperature type of serpentinizing system that operated away from magmatic intrusions that bore most directly on the emergence of life [26,43]. The discovery in the year 2000 of the so-called Lost City springs 15 km distant from the mid-Atlantic Ridge gave credence to this hypothesis. Such hydrothermal convection cells operate at a probable maximum temperature of 150°C [25,44,79–81] and are driven by heat residing in the crust *and* by exothermic reactions—a further example of an engine feeding off its own output. A deeply penetrating near vertical fracture might well have begun the process away from ocean spreading centres [82]. The hydrothermal convection progresses through the generation of cracks at scales ranging from kilometric to nanometric, dominantly in response to tectonic stress at the larger scales and through positive feedback involving increases in pore pressure, chemical alteration and the force of crystallization at the smaller scales, and finally through diffusion in the rock matrix. Such feedbacks explain why the Lost City hydrothermal system appears to have continued operation for at least the past 30 000 years (or in more appropriate units for the emergent processes under consideration,  $10^{17}$   $\mu\text{s}$ ) [83]. The solutions produced in this process are thermostated (approx. at 150°C) by the brittle-to-ductile transition through serpentinization, whereas their pH is buffered to around 11 by the precipitation of magnesium hydroxide (the mineral brucite), and some cations (mainly calcium) are released to solution to balance charge [84,85]. At the same time, ferrous iron in olivine reduces some of the water to

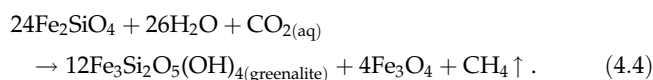
hydrogen as shown in this highly simplified reaction [85]:



Similar reductions [86–88] are responsible for methane generation from carbon dioxide idealized as:



and

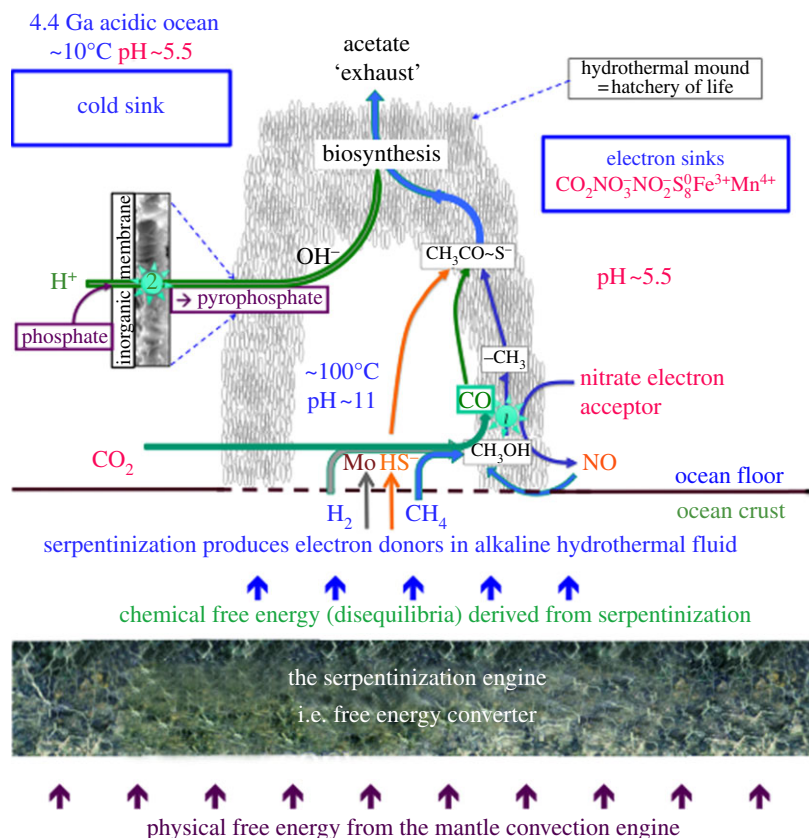


While these reactions progress rapidly at high temperatures [89], the methane:hydrogen ratio increases at lower temperatures as shown by Etiope *et al.* [90] using isotopic analyses of carbon and hydrogen. Substantial methane emanating from deeper within the crust is also added to the convecting solutions from below [44,90–94] (figure 3). The methane, formate and hydrogen emerging in the lower-temperature serpentinization effluents then provide the electron-donor fuels offered at the emergence of life. Other constituents released or generated during lower-temperature serpentinization are bisulfide ( $\text{HS}^-$ ), ammonia and molybdenum and tungsten as  $\text{Mo}^{\text{IV}}/\text{W}^{\text{IVS}}/\text{Se}_{3-x}\text{O}_x^{2-}$  or  $\text{Mo}^{\text{VI}}/\text{W}^{\text{VLS}}/\text{Se}_{4-x}\text{O}_x^{2-}$  [102–107].

A point to note here is that it is largely in the process of serpentinization that the cascade of dissipation engines relieving the Earth of its heat burden makes the fateful transition from largely physical to largely chemical FEC engines. That is, the serpentinization process primarily converts physical disequilibria, in the form of mechanical stress and thermal gradients, to the production of structural, mineralogical, and most notably, chemical disequilibria—all of which then serve to directly set the table for the emergence of life.

## 5. The vehicle for the first metabolic free-energy-converting engines: turnstiles and electron bifurcators

Extant life works largely through the operations of remarkable nano-devices [108], many of which are merely clever equilibrium mechanisms functioning as catalysts, switches and passive carriers (e.g. haemoglobin [109], aconitase [110] and *lac*-repressor [111]). However, those that mediate the critical, but inherently non-equilibrium activity of free energy conversion, i.e. function as engines, form a functionally distinct class. And, because this is the class of nano-devices that concern us here, and that we are seeking to find at work in the ‘lost cities’ of the Hadean, we need to ask what sorts of nano-device mechanisms are required to effect chemical free energy conversion. Here, the picture is not entirely simple. Most analysed examples of biological devices in the engine class have proved to depend critically on physically moving parts (cavities and passages that open and close, parts of proteins that move relative to each other, etc.). These include, redox-driven proton pumps [112], rotor–stator type ATPases [113–115] and all other motors [116], and membrane-integral



**Figure 3.** The final cascade of engines leading to the emergence of life. The mantle convection engine (figure 2) delivers heat to the near surface and stresses the crust to effectively feed the serpentinization engine. The photographic montage of a typical, scale invariant example of serpentine, offers us a gallery view of the composite engine responsible for driving life into being. The olivine-rich crustal rock fractures in response to the convective stress. The initial fractures propagate and anastomose as carbonic ocean water gravitates to depth and interacts with the hot rock. The hydrodynamic pressure increases the effective stress while at the same time exothermically oxidizing, carbonating, hydrating and hydrolysing the mineral constituents so allowing further access of water to rock. The force of crystallization causes large-scale expansion of the rock body, further fracturing and lowering the density of the rock, leading to diapirism and yet further fracturing. Apart from the physical free energy released as heat [95] by this disorganization, chemical free energy is also released, particularly at the propagating fracture tips. Here fresh iron–nickel-bearing mineral surfaces reduce water to hydrogen, whereas carbon dioxide is reduced to formate and methane, fuels for emerging life [44,96–98]. At the same time, calcium and some magnesium and sulfide ions are released to the fluids rendering them highly alkaline. Temperature is regulated by rock strength at the base of the cell while pH is buffered to approximately 11 units by brucite ( $\text{Mg}(\text{OH})_2$ ). This well-ordered hydrothermal effluent is driven convectively to the ocean floor where, on interaction with mildly acidic ocean water, porous mounds comprising iron–magnesium hydroxides and silicates, iron–nickel–cobalt–molybdenum sulfides and ephemeral iron–calcium–magnesium carbonates are precipitated [24,25,99]. We argue here that some of the marginal compartments, subjected to redox, pH and thermal gradients, assemble natural engines to dissipate these disequilibria while driving endergonic (anti-entropic) reactions: (i) a nickel/iron/molybdenum sulfide engine reducing  $\text{CO}_2$  to  $\text{CO}$ , (ii) an electron bifurcating mixed valence molybdenum-bearing iron sulfide composite engine dissipates redox energy through the reduction of nitrite while oxidizing hydrothermal methane and reducing oceanic carbon dioxide, resulting in the generation of activated acetate [46], (iii) a pyrophosphatase engine comprising green rust interlayers [100,101] that clamp contiguous orthophosphates ( $2 \times \text{HPO}_4^{2-}$  or  $\text{Pi}^{2-}$ ) in a natural metal ion mediated binding site where they condense, only to be released in the proton flux [19].

pyrophosphatases [117–119]. On the other hand, such moving-parts mechanisms are not inherently required for chemical free energy conversion and, as we argue here, may well not be directly involved in electron-bifurcation—one of the two classes of FEC devices that we here propose got life started. Even in that case, however, moving parts mechanisms may have had a role to play which is not unlike the role they have been seen to play in the analysed examples of electron bifurcating engines, such as the Q-cycle protein complex [120]. Furthermore, the other class of FEC devices which we believe was necessary for life's emergence does appear to inherently require moving parts mechanisms as we discuss below. These considerations argue strongly that if we must identify abiotic devices that could serve as the first engines of chemical free energy conversion to power, the first steps in the launching of life, then they will likely be found in physical settings that could provide, among other things, the right kind of controllable physical flexibility and movable parts.

But finding such devices in an abiotic world seems a daunting challenge, so it is worth pausing to ask whether this is really one we have to take on. Is the right model of the emergence of life an 'engines-first' one; that is, do we really need FEC engines, as we are here supposing, just to initiate the very first steps in the transition to life? And then if we do, is it really feasible that the mineralogical constructions within the alkaline hydrothermal mounds could provide the controllable moving parts that most, if not all, biologically relevant chemical free energy conversion seems to require?

As to the first point, the fact that all extant life is, and inherently depends on being, a far-from-equilibrium physical system, in both structure and process, makes it hard to believe that it could ever have been otherwise. However, in the production and maintenance of this far-from-equilibrium system, the second law requires that life is essentially a construct of FEC engines—all the way up as well as all the

way down. These considerations support the proposition that FEC engines were the essential enabling inventions at life's very onset, although this is admittedly not the general view of the matter. The question, of course, comes down to whether life can begin exclusively with chemistry operating at (or very near) equilibrium. If the answer is no, then some reactions must be driving significantly away from equilibrium, driven, that is, in spite of being endergonic, and this, by the second law, inescapably requires that they be coupled to a thermodynamically larger exergonic reaction via an FEC engine.

If we need, for example, an ATP-like diffusible source of free energy at the start, such as would be provided by pyrophosphate in disequilibrium with respect to its hydrolysis products, then we inescapably need to have that disequilibrium produced (and maintained) by being coupled to some external source of free energy via an engine (note that it is the posited *disequilibrium* that alone makes pyrophosphate—or anything else—a source of free energy for driving other reactions; pyrophosphate at equilibrium with its hydrolysis products, no matter its concentration, is exactly useless as a source of driving free energy). Or if we need, at the start, some form of fixed carbon at levels above equilibrium with its oxidation products, or produced by a path that involves an endergonic step, then we again must find an engine that can couple these anti-entropic processes to a driving source of free energy. Equilibrium chemistry, no matter how facilitated by catalysts, or shifted by the manipulation of reactant concentrations, is prevented in principle from filling this bill. That is, if proto-life requires any non-equilibrium states to be maintained, as we argue here, then it must have invented true engines for the purpose that were fed by the geochemically given sources of free energy (disequilibria) and which had as their work output the needed non-equilibrium states [8,46,121]. For this purpose then, toying with the thermodynamic parameters of simple equilibrium reactions, whatever the context, is not going to help. Instead, we argue, FEC engines, including both chemiosmotic and electron bifurcating engines, coming into play right at life's emergence—if only we could divine how they might have done so—would explain how the essential, but thermodynamically anti-entropic first steps (i) to carbon dioxide reduction via exergonic steps, (ii) methane oxidation, and (iii) phosphate condensation being driven far from equilibrium with respect to phosphate, could be made to happen. Given these three particular challenges, we first outline the hydrothermal environment, vouchsafed by serpentinization, in which particular free energy sources are on offer in the form of steep chemical, redox, pH and thermal gradients. We later return to the question of whether the vent precipitates might provide the kind of controllable flexibility devices that are found functioning as the beating heart of nearly all extant biological FEC devices.

Upon exhalation, the alkaline and reduced hydrothermal fluids at approximately 100°C interacted with the acidulous, somewhat oxidized, ocean [122] to precipitate porous inorganic mounds [123–125]. The main precipitates consisted of silica, silicates, oxyhydroxides, phosphates and ephemeral carbonates, and, in cases where bisulfide was exhaled, metal sulfides (figure 4). Mixed valence iron (nickel) sulfides (mackinawite and the thiospinels, greigite and violarite) and iron oxyhydroxides (green rust) dominated the mineralogy [128–136]. It is worth noting in passing that mackinawite, violarite and greigite have structures generally affine with the active centres of hydrogenase (CO

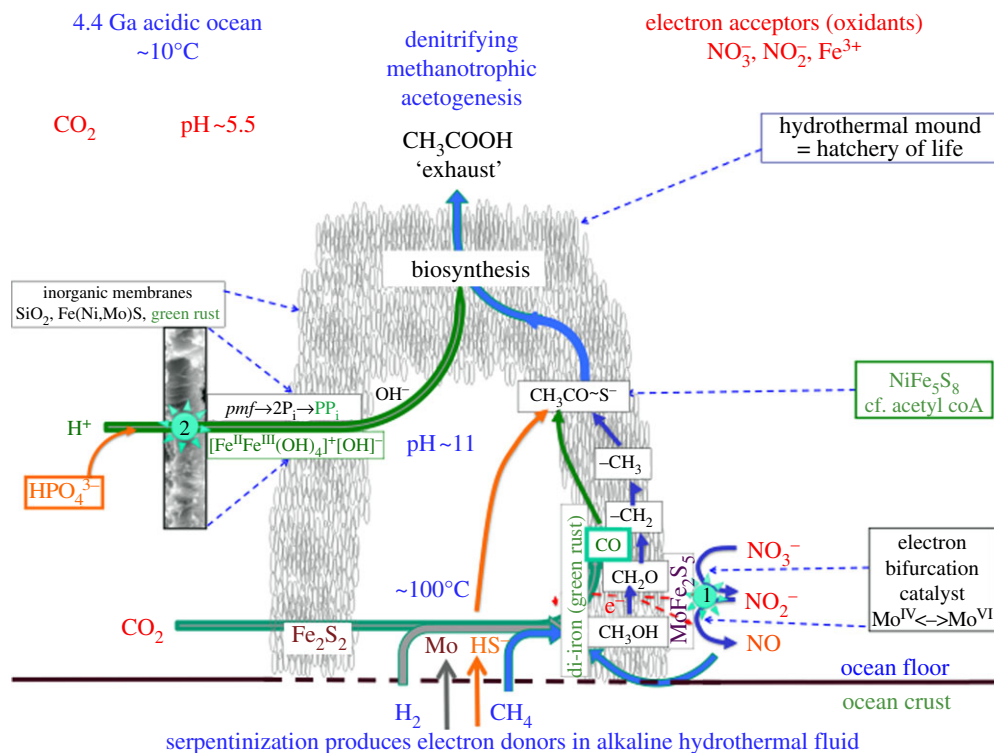
dehydrogenase (CODH) and acetyl coenzyme-A synthase (ACS)), whereas green rust has a similar structure to di-iron methane monooxygenase [19,126,133–136].

In laboratory simulations, pore volumes of the inorganic precipitates ranged between 10 and 1 ml, and the compartment walls were from 4 to 100 µm thick (figure 4) [123]. The silica, calcium, magnesium, carbonate, phosphate and most of the transition metals such as iron, nickel, cobalt, zinc and tungsten making up these inorganic membranes were contributed from the ocean, while sulfide, trace molybdenum (as  $\text{MoO}_4^{2-}$ ) and additional calcium, magnesium and trace tungsten were carried in the alkaline hydrothermal solution [25,71,81,103–105,122–125]. In their various forms and compositions, the compartmentalized precipitates or bubble cells tended to keep the two contrasting solutions apart and far from equilibrium. Steep chemical, redox, pH and thermal gradients were imposed across the inorganic membranes comprising the outermost compartments of the hydrothermal mound. Iron was precipitated in multiple distinct, chemically reactive forms, many of them of mixed valence. Initially, these comprised ferrous iron as ephemeral siderite ( $\text{Fe}_2\text{CO}_3$ ), as ferrous hydroxide ( $\text{Fe}(\text{OH})_2$ ) and mackinawite ( $\text{FeS}$ ), but were oxidized along the outer margins of the membrane to green rust, expected to range in composition from approximately  $[\text{Fe}_4^{\text{II}}\text{Fe}_2^{\text{III}}(\text{OH})_{12}]^{2+}[\text{CO}_3\cdot 3\text{H}_2\text{O}]^{2-}$  and/or approximately  $[\text{Fe}_3^{\text{II}}\text{Fe}^{\text{III}}(\text{OH})_8]^+[\text{Cl}\cdot 2\text{H}_2\text{O}]^-$  through to approximately  $[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{OH})_4]^+[\text{OH}]^-$ ; to oxidized mackinawite containing some  $\text{Fe}^{\text{III}}$ ; then to greigite (approx.  $\text{SFeS}[\text{Fe}_4\text{S}_4]\text{SFeS}$ ) [100,123,128–131,133–136] or violarite (approx.  $\text{SNiS}[\text{Fe}_2\text{Ni}_2\text{S}_4]\text{SNiS}$ ) [129,132] associated with minor clusters of iron–molybdenum sulfide ( $\text{Mo}^{\text{IV}/\text{VI}}\text{Fe}_2\text{S}_3^{0/2-}$ ,  $\text{Mo}_2^{\text{IV}/\text{VI}}\text{Fe}_3\text{S}_9^{0/2-}$  or  $\text{Mo}_3^{\text{IV}/\text{VI}}\text{Fe}_5\text{S}_{14}^{0/2-}$ ) [103–105,121,125]. First, we turn to the fixation of carbon.

## 6. The carbon-fixing engine and the role of electron bifurcators

The electron-donating fuels that were fed continuously to the compartmental interiors from the alkaline hydrothermal solution were methane, hydrogen and minor formate, whereas the potential oxidants in the all-enveloping ocean were carbon dioxide, nitrate, nitrite, sulfite, native sulfur and ferric iron [25–27,43–45,54–56,81,90,125,137–141]; cf. [142]. Additional potential free energy sources were provided by the five units of pH (equivalent to approx. 300 mV) and the temperature contrast of around 50–80°C imposed across the mineral barrier separating the hot alkaline solution from the cool ocean [25,143]. These conditions were maintained over long periods by the chemical and thermal stability of the hydrothermal system and the ocean currents, augmented by secondary convection of ocean water driven by heat in the hydrothermal mound and its entrainment in the exhaling flow [8]. In cases where there was a natural narrowing of the mound, the *venturi* effect would come into play, autocatalytically sucking the external solutions inwards much in the manner of a carburettor [140]. Flooding of the system was obviated by the precipitation of further inorganic compartments. Thus, the hydrothermal mounds were *de facto* free energy and material capturing devices that offered a surplus of opportunities for electron bifurcations, catalysis, reactions, interactions and engine assembly across those inorganic membranes constituting their outer margins.





**Figure 4.** Diagram to show how the entropic output from serpentinization fuels an emergent metabolic engine within the concomitantly precipitated alkaline hydrothermal mound with methane and hydrogen, augmented by pyrophosphate condensation driven by the ambient proton motive force. The natural titration of the alkaline hydrothermal solution with the acidulous ocean leads to precipitation of chemical garden-like compartments. A secondary acidulous ocean current bearing the oxidants is convectively driven by heat emanating from the mound and also pulled upward by entrainment in a manner comparable to a carburettor so that the reductants—delivered at a similar rate to the oxidants—are partially oxidized to organic intermediates [8,26,46]. Reactions are catalysed by the (dislocated) surfaces of transition metal sulfides or in the interlayers of green rust acting here as a di-iron methane monooxygenase [19,126]. The specific model engines argued here to have driven the first metabolic pathway are (i) electron bifurcation on Mo-sulfides reduced by  $H_2$  in a two-electron reaction but ejecting these electrons in a gated manner towards a high potential acceptor (such as nitrate or nitrite) and a low potential iron–nickel–sulfur-containing mineral such as violarite [19,104,127]. This low potential mineral is considered to achieve reduction of  $CO_2$  to  $CO$  in a reaction reminiscent of that at the catalytic metal cluster of CO-dehydrogenase (CODH); (ii) positive redox feedback loop in the reaction sequence from  $CH_4$  through  $CH_3OH$  to  $CH_2O$ .  $CH_4$  activation towards integration of an oxygen atom (resulting from  $NO$  produced by engine 1) requires reducing equivalents which are provided by the (lower midpoint potential) subsequent oxidation step of  $CH_3OH$  to  $CH_2O$ ; (iii) condensation of the two C1-moieties issued from the high and low potential branches (i) and (ii) into acetate or an acetyl moiety on greigite [19,46]; (iv) a pyrophosphatase engine comprising green rust interlayers where water activity is close to zero, opens at the oxidized exterior through positive charge repulsion as the ferrous iron is oxidized (figure 5) [100,101], allowing protons access to the interior which pull orthophosphates by charge attraction ( $2 \times HPO_4^{2-}$  or  $P_i^{2-}$ ) into the subnanometric compartments. Clamped by the ferric iron atoms bordering the walls of the interlayers, neighbouring orthophosphates condense to the pyrophosphate (which has an overall lower charge as  $HP_2O_7^{3-}$  or  $PP_i^{3-}$ ) on interaction with protons. The flux of the remaining protons drives the pyrophosphates towards the rear exit of the green rust nanocrysts where they phosphorylate organic intermediates produced by engine 1.

However, the theoretical challenge is to work out how a metabolism was engineered naturally in this seemingly appropriate vehicle. We argue that the challenge mainly amounts to discovering the specific free energy conversion mechanisms that would have coupled the available sources of free energy discussed earlier to the production of fixed carbon. In spite of the obvious difficulties, we do not consider the quest to be hopeless. After all, these same tensions play central roles throughout extant life. First of all, in essentially all cells the generation and use of  $H^+$  or  $Na^+$  chemiosmotic potentials stands at the centre of their energy metabolism. And, most notably in the present context, the majority of autotrophic microbes hydrogenate carbon dioxide with the help of the free energy supplied by either the chemiosmotic proton or sodium motive force [144–146]. The methanogens and the homoacetogens, frequently put forward as likely ancestral types of carbon fixation, manage the hydrogenation of carbon dioxide through somewhat different formulations of the acetyl coenzyme-A pathway, both driven in the reductive direction [147]. Yet, the overall energy available between

the  $H^+/H_2$  and the  $CO_2/HCOOH$  couples used by these prokaryotes is at the lower limit of viability [46,148]. Moreover, laboratory experiments involving the reduction of carbon dioxide in aqueous conditions, even when driven electrochemically, normally stall at formate [149]. Remembering that the onset of free energy conversion has to conjure with a high initial threshold of operation [7,150], it therefore seems unlikely that the methanogens and the homoacetogens, at least as they operate today, were the first metabolists when there was so little redox energy available to them. Given this marginality, how could comparable pathways to carbon fixation have arisen and functioned—especially in the absence of the complex enzymatic and co-factor assistants on which they now depend?

In response to this question, Nitschke & Russell [46] have suggested a different way to crank up the first metabolic engine—one that is driven from either end of the acetyl CoA pathway, thus obviating the need to assail the steep endergonic (anti-entropic) gradient to formaldehyde. Fixation of carbon may have occurred abiotically in single steps

through the initial generation of two critical reagents, a (thiolated) methyl group and carbon monoxide, which then reacted to form acetate. In this scheme, both these intermediate products are respectively derived from methane and carbon dioxide through the double use of electron bifurcation mediated by a molybdenum atom. The redox midpoint potential of the  $\text{CO}_2/\text{CO}$  couple is approximately  $-700$  mV at pH 11, that is, very likely at best, isopotential with the  $\text{H}_2$ -imposed ambient redox potential in the hydrothermal settings described earlier. The carbon dioxide conversion to carbon monoxide would therefore be roughly in thermodynamic equilibrium. Extant life reduces carbon dioxide to carbon monoxide at a nickel-containing Fe–S cubane in close proximity to a single iron atom, the so-called C-cluster (CODH of ACS), which apparently is sufficiently negative to achieve reduction of carbon dioxide to carbon monoxide. However, how does this cluster become reduced in the first place in organisms using only  $\text{H}_2$  as reductant? The concentrations of  $\text{H}_2$  as well as the pH values prevailing around an extant cell would certainly yield far less reducing power than that found in the hydrothermal mound. Nevertheless, life obviously manages to quantitatively reduce the C-cluster. It has recently been shown that this redox feat is achieved by electron bifurcation [151]. As some of us have outlined previously [46,121,125], electron bifurcation is an entropy-decreasing device par excellence. Although, in extant life, the bifurcating redox centre used in boosting reducing power to these negative potentials is an organic molecule, flavin, this role in the mound is likely to have been played by the two-electron transferring metals molybdenum or tungsten as argued earlier [121,125]. However, what may have been the oxidant ultimately necessary to enable redox bifurcation? Several possible candidates come to mind such as  $\text{Fe}^{3+}$ ,  $\text{Mn}^{4+}$ , sulfur, sulfite or oxidized nitrogen compounds [25,46,139–142]. Although all of these may have played a role, we assume that nitrate and nitrite were likely to have been crucial because they provide both an electron sink and a source of oxygen for the conversion of methane to methanol as detailed below [139]. The engine 1 in figure 4 therefore likely was a Mo/W-containing mineral, ratcheting electrons onto carbon dioxide and driven by the oxidizing potential of the nitrogen oxyanions, nitrate and/or nitrite.

Now, carbon monoxide is an extremely reducing molecule with a redox midpoint potential that was certainly more negative than that of the mound environment. This spells trouble because it implies a high tendency to quickly re-dissipate the temporarily lowered entropy. We assume that this re-dissipation is prevented, just as in extant life, by the immediate reaction with a methyl group or methanol molecule derived from the oxidation of methane and its thiolation [152,153]. The concomitant functioning of both pathways, one reducing and one oxidizing, therefore is indispensable for stabilizing the entropy decrease achieved by generating the out-of-equilibrium carbon monoxide molecule [46]. This brings us to a seeming contradiction. Although the redox state of carbon, indeed, becomes more oxidized when going from methane to methanol, this reaction is more than a simple redox conversion. In fact, (mildly reducing) electrons are required to activate nitric oxide molecules, so that an oxygen atom from nitric oxide can be integrated in the strongly chemically inert methane moiety. The sum reaction of methane and nitric oxide to yield methanol and nitrous oxide therefore requires two electrons rather than providing reducing equivalents. To produce a (volatile) nitric oxide molecule from nitrite, two more electrons are needed.

From the redox potential of those two reactions (more than 0 mV),  $\text{H}_2$  can in principle do the job or at least get the reaction going. Of course, methane to methanol conversion can also participate as oxidant in the bifurcation reaction driving carbon monoxide production. Methanol in extant life is then oxidized to formaldehyde, a true oxidation reaction liberating electrons. Significantly, the reducing power of the liberated electrons is sufficient to feed the activation of an oxygen atom in the preceding step from methane to methanol and this is what it does in extant life. We consider that this positive feedback coupling of the first two steps in methane oxidation involving the concomitant reduction of green rust represents another type of engine lowering the entropy of the system. Formaldehyde can then be re-reduced by one electron to yield a methyl group, presumably attached to a sulfenyl-function. The methyl will then be condensed with carbon monoxide, finishing the job of transforming the out of equilibrium carbon monoxide into the carbon moiety, acetate.

The activated acetate could now provide for biosynthesis. The methyl sulfide acts here in a similar manner to acetyl coenzyme-A itself, and the mechanism, while obviating the need to transit all the intermediates along the acetyl coenzyme-A pathway, produces a molecular analogue of the thioester central to much of biochemistry [46,152]. We have termed this putative first metabolism 'denitrifying methanotropic acetogenesis' [46]. Further hydrogenations and carboxylations of the acetyl thioester, catalysed by iron sulfides, could produce the higher carboxylic acids, through pyruvate to succinate in the incomplete reverse tricarboxylic acid cycle. And Huber & Wächtershäuser [154] have demonstrated the reductive amination of some of the carboxylic acids to the corresponding amino acid catalysed by iron monosulfide or ferrous hydroxide, just the fine mineral precipitates to be found in membranes comprising the outer surfaces of the hydrothermal mound [122]. Were the thioester to be phosphorylated, the activated acetate could now provide for some of the early bioenergetics as well as for further biosynthesis [155]. This then brings us to the issue of how the necessary pyrophosphate disequilibrium could be produced abiotically in the mound's membrane structure.

## 7. A pyrophosphatase engine: chemiosmosis for free

Let us first emphasize that we are not here seeking a way to efficiently condense orthophosphate to pyrophosphate as a presumed equilibrium reaction (e.g. by catalysis, or raising the concentration of orthophosphate), but instead a way to drive this endergonic reaction far from where it would be at equilibrium. We need this not just, or not primarily, to produce a sufficiently high concentration of pyrophosphate to act as a *reagent* in subsequent reactions, but specifically to produce a pyrophosphate/orthophosphate *disequilibrium* which can then function as a free energy source (not a reactant source) for driving downstream endergonic reactions—reactions such as the phosphorylation of the thioester mentioned earlier. But to achieve this, the second law dictates, we need an FEC engine that can couple the dissipation of some available free energy source to the anti-entropic production of pyrophosphate. If, as seems most likely, we assume that at the emergence of metabolism the driving disequilibrium for this process was the geochemically provided proton gradient

discussed earlier, then we are seeking a mechanism that acts in similar manner (albeit in reverse) as has recently been proposed for the membrane-integral  $K^+$ -dependent  $H^+$ -pyrophosphatase from *Vigna radiata* [118] and from the homologous  $Na^+$ -pyrophosphatase from *Thermotoga maritima* [119].

The mechanism put forward in these two papers provides a detailed description of a molecular device that electromechanically ties the hydrolysis/condensation reaction inter-converting between pyrophosphate and two orthophosphates to the transport of a proton or a sodium ion across the membrane in which the device is embedded [118,119]. The essential feature of this linkage in condensations is that it makes each of the two processes conditional on the other—and with a specific logical directionality, namely, a proton (or sodium ion) can pass from outside to inside if, and only if, that happens coincidentally with the condensation and release of a molecule of pyrophosphate, or conversely, a proton (or sodium ion) can pass in the opposite direction, if and only if that happens coincidentally with the hydrolysis of a pyrophosphate and the release of the orthophosphate products. Because of this coupling logic, the device can function as a reversible free energy converter; converting, for example, the controlled dissipation of an outside-to-inside proton gradient in the production of a disequilibrium in the concentration of pyrophosphate versus orthophosphate (i.e. acting as a proton-gradient-driven pyrophosphate synthase). Or it can function equally well in reverse as a proton-pumping pyrophosphatase. Which way it goes depends, of course, on which way yields a net negative change in free energy (equivalently a net positive rate of entropy production).

What is most remarkable about the mechanism as proposed by Lin *et al.* [118] and Kellosalo *et al.* [119] and also most important for our present goals, is its stunning simplicity wherein controllable flexibility is the key device. In particular, a flexible passageway through the protein can open and expose an internal cavity alternatively to either side of the membrane or close it off to both sides. These flexing motions are controlled by whether charged residues judiciously positioned along the walls of the passageway are neutralized or not by binding an appropriate counter-ion involved in the process (e.g. a proton, or an orthophosphate ion). As proposed, the device steps sequentially through a series of five configurations, or states (in the manner analysed at length in such famous treatises on free energy transduction as those by Caplan & Essig [156] and by Hill [157]) and translocates one proton and catalyses one pyrophosphate synthesis (or hydrolysis) per cycle.

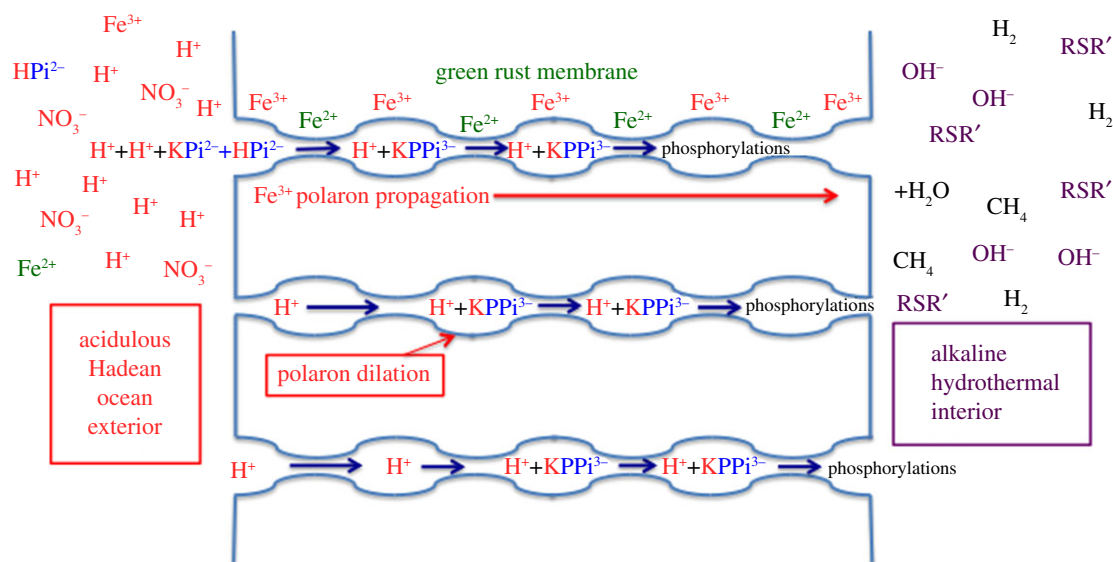
This mechanistic simplicity is all the more arresting, because the device performs an FEC function that is exactly parallel to that carried out by the rotary ATP-synthases, which famously stand at the apex of complexity and sophistication of design as engines of free energy conversion (and operates much the same way as the Wankel engine [115]). But it also, quite obviously, makes very much less daunting the task of finding abiotic versions of a device of this kind in the mineralogy of the serpentine effluent mounds. We discuss this issue next and lay our reasons for thinking that the mineralogy of the membranes formed in the alkaline hydrothermal precipitates is a great deal more promising as a context in which chemiosmotically driven  $PP_i$  synthase activity could arise abiotically than one would at first have any reason to suspect.

When sulfide is present as  $HS^-$  in the alkaline hydrothermal solution the inner zones of the precipitated membrane comprise mackinawite and subordinate greigite nanocrystals,

while the outer zones comprise ferrous hydroxide [123] which would oxidize in steps, on reaction with nitrate, to green rust (e.g. approx.  $[Fe_3^II Fe^III(OH)_8]^+ [Cl_2 \cdot 2H_2O]^-$  and approx.  $[Fe^II Fe^III(OH)_4]^+ [OH]^-$ ) to form a well-ordered, variable valence platy mineral arranged orthogonally to the membrane outer surface, just as mackinawite tends to be oriented normal to the inner surface (figure 4) [123,133–136]. The interlayers between these platelets offer subnanometric compartments in which water activity is vanishingly low. In a prescient and brilliant paper Arrhenius [100] notes that as green rust forms, the ferrous hydroxide layers are forced apart by the ferric ions, admitting counter-ions such as chloride in the company of water molecules. This layer of water molecules is clamped between two catalytic surfaces that, while highly viscous, could permit the persorption of larger anions such as the di-anion carbonate to replace the chloride or hydroxide ions in a compartment that still would be less than a nanometre wide. At relatively low pH, orthophosphate might be accommodated together with phosphate-charged reactants between these flexible nanometric membranes [100,158–160]. These tiny channels have the potential to provide primitive enzymatic functions. To quote Arrhenius, 'Like cells, they retain phosphate-charged reactants against high concentration gradients and exchange matter with the surroundings by controlled diffusion through the 'pores' provided by the opening of the interlayers at the crystal edges. Here, the exposed negative charge on the interrupted metal hydroxide 'membrane' leads to sorption of cations as 'gatekeepers' [100].

The challenge is to imagine how these naturally provided subnanometric channels might be put to the specific conversion work that needs to be done. For example, can comparisons be made with the pyrophosphatases mentioned earlier [118,119]? These so-called membrane-integral or M-PPases couple pyrophosphate hydrolysis or synthesis with sodium ion or proton translocation. The M-PPase has a negatively charged gate comprising a hinged lysine swinging between an aspartate and a nearby glutamate residue. The gate can be opened or closed by a simple binding-change mechanism, and below the gate is an exit channel. In the case of a putative green rust pyrophosphatase, a possible analogous mechanism might come about as follows: an initially open, i.e. relatively oxidized, channel facing the membrane exterior might take up and spatially confine orthophosphates from the acidulous ocean, partially neutralizing the local charge configuration within the channel as it does so and causing the channel to contract locally; this change might form a gated, active cage, forcing the condensation of pyrophosphate. As in the case of the protein examples, this condensation would be expected locally to reduce the overall charge, initiating a local positive charge repulsion, and freeing the pyrophosphate to the interior membrane environment—with a bias in that direction being ultimately due to the proton gradient. The newly minted pyrophosphate could then phosphorylate distal carboxylates of organic molecules freshly generated on iron–nickel sulfides comprising the membrane's interior, i.e. in the carbon-fixing engine.

We attempt to make this general model a bit more specific, and plausible, in the following discussion. As previously mentioned, green rust of the kind to be precipitated at the interface between the alkaline hydrothermal solution and acidulous phosphate and iron-bearing ocean water is likely to comprise  $[Fe_3^II Fe^III(OH)_8]^+ [Cl_2 \cdot 2H_2O]^-$  and  $[Fe^II Fe^III(OH)_4]^+ [OH]^-$  [161–166]. Officially named fougérite [163], the mixed valence mineral reacts rapidly and reversibly



**Figure 5.** Speculative physical model of a putative green rust (fougerite  $H^+$ -pyrophosphatase) [cf. 117–119], based on the generation within the mineral interlayers of redox polaron ‘quasi-particles’—manifest as localized channel dilations—that can propagate in a directed manner along the interlayer. Boundary conditions are given by the bathing of the outside of the iron hydroxide membrane in an aqueous solution of protons, carbon dioxide, nitrate and ferric iron (the Hadean Ocean simulant) while the inside, iron sulfide zone of the membrane, is bathed in hydrogen, methane and bisulfide (the alkaline hydrothermal solution simulant). The transmembrane potential—part redox and part pH gradient—totals approximately 1 V [19,140,148] and provides the vectorial free energy that drives the system’s inherently endergonic processes: (i) the generation and inward propagation of localized, polaron-based, channel dilations, (ii) the confinement of phosphate under conditions of reduced water activity within a superficially positioned local dilation, (iii) the subsequent condensation to pyrophosphate which in turn permits the mobilization of the polaron dilation and (iv) the ‘pumping’ of the pyrophosphate into the interior against its own gradient. The ferrous hydroxide comprising the outer margins of the precipitate membrane begins to be oxidized by nitrate to green rust which has the effect of opening the interlayers locally as the ferric ions on either side of the interlayer repel each other, the positive charges attracting counter-ions such as chloride, nitrate, carbonate and phosphate to take up the space [100,101,135,136,163–165]. The changes in local redox state locally distort the crystal structure inducing, via phonon interactions, the formation of localized polaron quasi-particles [171,172]. The polaron-based local dilations produced by the oxidation of green rust migrate through  $Fe^{3+}$  hole polaron transport, charge hopping interdependently correlating with anion migration along the interlayer towards the interior [173]. The double valent anions such as orthophosphate ( $Pi^{2-}$ ), confined within localized polaron distortions, are also pushed along the interlayer (acting like a protein channel or pore) which thereby acts as a peristaltic pump. Condensation of the phosphates to di- or polyphosphates takes place in the confined space of a single polaron dilation positioned at the external interface within the channel where water activity is low, in a reaction involving one proton and the generation of one water molecule per condensation and the consequent lowering of charge, thereby releasing the grip of the electron field and allowing the subsequent release of the condensed phosphates to the interior [100,108,140,159,171,173–175]. Re-reduction of the same green rust is through the oxidation of the hydrothermal methane and hydrogen (figure 4).

to redox conditions between ferrous (approx.  $Fe_2^{II}Fe^{III}(OH)_7$ ) and ferric fougerite ( $Fe^{II}Fe_2^{III}(OH)_8$ ) with the obligate intercalation of anions to maintain charge balance [160–165]. Such a nanocryst may have acted as the pseudo enzyme driving phosphate condensation in lieu of the membrane helices [100,165,167–169]. The monovalent interlayer anions drawn in to balance charge in these varieties of green rust are more easily exchanged than the divalent ions such as sulfate and carbonate [165,168], and are thus more susceptible to replacement by active phosphate sorbents [169,170]. We hypothesize that a proton flux, driven by the pH gradient amounting to five pH units, could translocate the orthophosphate anions from the ocean bathing the mound into the open subnanometric chambers walled by the crystal planes which tend to be oriented orthogonally to the outer and inner surface of the membrane (figures 4 and 5). For example, oxidation of ferrous hydroxide or further oxidation of green rust by nitrate towards the exterior (ocean side) of the inorganic membrane would have the effect of distorting the interlayers at their distal ends, opening them up to an influx of orthophosphate ( $HPO_4^{2-}$ ) from the Hadean Ocean [176], distortions that, as polarons, would migrate towards the membrane interior (figure 5). At the same time, the proton flux might be relied upon to push these counterions down the steep proton gradient into the reduced

interlayer where they would lodge, so blocking the proton flux [26]. Once contained in these interlayers, the orthophosphates are condensed to various pyrophosphate species such as trimetaphosphate [167,169], with the proximal ferrous iron atoms acting in the same role as the five magnesium ions that neutralize phosphate–phosphate repulsion, packed closely around the phosphates in the  $H^+$ -pyrophosphatase described by Lin *et al.* [118]. Such diadochic substitution has been demonstrated by Athavale *et al.* [177] whereby ferrous iron substitutes for magnesium in clamping phosphates in RNA conformations in the Group I intron P4–P6 domain of *Tetrahymena thermophila*. The interlayer water molecules in the oxidized end-member of fougerite should permit proton hopping from water molecule to water molecule via a Grotthuss-type mechanism much as they do in the exit/entry channel to the extant enzyme [119,178,179]. One of the protons would aid in the condensation in a reaction that also produced a water molecule.

The build up of protons would drive the further condensation of contiguous orthophosphates to the lower-charged pyrophosphate ( $HP_2O_7^{3-}$ ) but at the same time would oxidize the reduced iron (with the concomitant production of hydrogen) [137]. The now more oxidized confining walls of the interlayer would retreat and lose their grip on the pyrophosphate so that the activation energy required to drive

protons down gradient would be substantially lowered [171,172]. The protons would push the pyrophosphates through the remaining portion of the interlayer or channel, releasing them for biosynthetic interactions such as the condensation of amino acids to peptides promoted by alkaline conditions [180–183] (figure 5). This system functions as an FEC, converting the dissipation of the transmembrane chemiosmotic disequilibrium into the creation of a pyrophosphate chemical disequilibrium on the inside. It achieves this by making proton translocation and pyrophosphate condensation mechanistically gated by, and thus reciprocally conditional on, each other. This action in turns depends on the formation of local, redox-driven, polaron-based structural dilations in the mineral interlayer spaces. The essential operational logic of the engine is that a proton cannot pass through the interlayer channel from the exterior to the interior unless it induces the condensation of phosphates taken from the exterior into pyrophosphate, which action permits proton and pyrophosphate to be driven together along the interlayer and ultimately released into the interior. Recharge of the green rust pyrophosphatase would be from electrons stemming from hydrogen or methane in the interior which would re-reduce the ferric iron in green rust resulting in electron hopping towards the exterior until they reached an unfilled metal site and polarized the neighbouring atoms and generated polarons [171]. Concentrations of polarons would produce phonons that would act as a low valence metal [171], distorting the green rust lattice so that it would regenerate ferrous iron on the green rust interlayer walls so that the ensuing orthophosphates would be re-gripped [173]. Once in a metastable state the redox conditions within the interlayer compartments would oscillate only within a limited range of ferrous : ferric ratios [162,173].

In this scenario, the translocation of pyrophosphate would only progress as a second proton is released to the membrane's interior. The very minimum theoretical  $H^+ : PP_i$  ratio thus would be 2. Surprisingly, just such a 2 : 1 stoichiometry has been calculated in the operations of  $H^+$ -pyrophosphatase in *Rhodospirillum rubrum*, whereas the  $H^+ : ATP$  ratio is 3.6 in the same bacterium [184]. Delivered from the green rust in such a manner the pyrophosphates could phosphorylate thioesters in further steps to biosynthesis as touched on in §6 on the founding of the acetyl CoA pathway mentioned earlier [24,46,148]. The only experimental support for comparable oligomerizations in mixed-valence double-layer metal hydroxide minerals has been provided by Pitsch *et al.* [158] and Krishnamurthy [185]. They have demonstrated the formation of tetrose-2,4-diphosphates and hexose-2,4,6-triphosphates from glycolaldehyde phosphate and pentose-2,4-diphosphates from glycolaldehyde phosphate and glyceraldehyde-2-phosphate, with ribose-2,4-diphosphate formed preferentially to other pentose-2,4-diphosphates.

## 8. A tandem of 'mineral' engines to start life?...

The purported redox-controlled phosphorylation outlined earlier might operate on the same nanometric green rust clusters as the redox changes associated with the oxidation of the methyl group and its re-reduction with electrons from a molybdenum cluster. Indeed, supposing these two engines, both involving green rust and working in concert, were enough to get a metabolism going within the inorganic compartments,

then a form of vertical reproduction might have led to ever more complex interactions. The inorganic cells grew, became sealed, then in response to hydrodynamic pressures, burst to spawn new contiguous cells. By such a process, any organic products from one compartment could be fed forward to the next. Thus, materials generated in the membranes of one cell could be entrained in the flow and born upward and concentrated in later cells, thereby reducing the permeability of the membrane as organic molecules, mainly peptides at first, acted as partial seals [74]. Therefore, these electrochemical gradients would be dissipated more effectively and new ones exploited. For example, Dieter Braun and co-workers [186–188] have demonstrated the effectiveness of a thermal gradient operating across a compartment's interior in concentrating charged organic molecules through thermophoresis, and we might imagine a natural electrophoresis sorting and ordering a range of these molecules in the membrane, the better for their subsequent interactions. With the drive from these additional engines, in time a Lamarckian evolution could, through the emergence of cofactors and a retroviral-like RNA [189,190], transform to a Darwinian evolution, and new engines approaching those mentioned at the start of this section could have emerged. And while still in the mound, perhaps the entire acetyl CoA pathway could have been sprung, allowing homoacetogens and eventually methanogens, access to the neighbouring ocean floor and ocean floor sediments and lava flows, inaugurating the deep biosphere [191–194].

## 9. ...And one-third to see it through to oxygenic photosynthesis?

At their core, of course, these great transitions are mediated by the emergence and evolution of new FEC engines. A newly published study of what is arguably the most consequential of these, the photosystem II (PSII) component of oxygenic photosynthesis, affords a beautiful insight into how complex and operationally precise the turnstile mechanisms at the heart of biological free energy converters can become [195]. The PSII engine couples the dissipation of the free energy of photo-excited electrons—the driving disequilibrium—to the oxidation (splitting) of water, liberating protons on the low pH side of the membrane, whereas the electrons are deployed to provide diffusible reducing equivalents and to take up protons from the high pH side of the membrane—which outcomes together make up the driven disequilibrium. The engine's deep challenge, however, is that it must oxidize two water molecules to produce one molecule of molecular oxygen—while properly dispensing four charge-separated electron/proton pairs—all in one cycle of the engine. In the cited study, it is shown that the two-water-molecule oxidation cycle proceeds through an eight-step sequence comprising a strictly controlled series of alternating electron and proton transfers, with each step being conditional on the completion of its predecessor.

This picture resolves the total cycle into four sequential instances of a base photon–electron–proton cycle. It is in this base cycle that the process-locking conditionality requirements of FEC in this system are first, and most importantly, imposed. The key issue is the constraint imposed by the system on the pathways by which the excited electronic state created by the absorption of a single photon can be

relaxed (and the system returned to its photoreceptive initial condition). Specifically, these constraints make this dissipative relaxation conditional on the coincident occurrence of the driven, i.e. endergonic, processes involved in the productive transfer of one electron, and then gated by that of one proton, from the manganese cluster and its surrounds possibly charged with two water molecules. In this way, the conversion of the photon's free energy to free energy stored in the proton gradient and in reduction potential, is achieved. The cited paper furthermore demonstrates that, as in the case of the other FEC engines thus far studied in sufficient detail, specific physical movements of the embedding proteins are apparently required to make the process work. In the present study, these are resolved as volume changes (attributable to coulombic effects resulting from shifts in the local charge configuration) associated in particular with the steps in the cycle involving proton translocations. It is finally worth noting in the present context that all of the charge transfer processes in the PSII cycle are mediated by a single  $\text{Mn}_4\text{CaO}_9$  catalytic complex comprising a 'distorted cubane' of structure rather similar to a mineral spinel, just as ferredoxins, ACS and CODH are comparable to a natural inverse spinel, inviting the thesis that such mineral structures were there for the taking from the respective environments by peptides and proteins as the first metabolists, and subsequently the first oxygenic photosynthesizers emerged [25,62,63,72–75,196–198]. Oxygenic photosynthesis effected a qualitative increase in processing by the biosphere at large [62,63] as the major high potential electron acceptor oxygen began to make itself felt at the great oxidation event and the eukaryotic world opened up, eventuating in the Cambrian and Devonian explosions [199–201].

## 10. Conclusions

We have attempted in this paper to describe and support a fairly detailed proposal as to where we need to look, and what we need to look for, in the attempt to understand how life emerged on this planet. This proposal traces the story through its physical and geological provenance, its history, its chemistries and mineralogy, and its sources of free energy. Finally, we have described how, in general terms, those sources of free energy must have become suborned to the support of the necessarily endergonic processes of pre-life through the action of abiotically produced mechanisms of free energy conversion. In this story, we have emphasized that the creation of life is but one piece, one component of creation, in the great order-creating industry that is the true business of our dynamic Universe. This order, whose creation is dictated by the thermodynamics of far-from-equilibrium systems, is everywhere in the form of auto-catalytic, work-creating engines—engines which accelerate, as active devices, the dissipation of the immense astronomy of disequilibrium with which our Universe was born. And we have seen how the engines of dissipation created in this way form a vast hierarchy of wheels within wheels, each wheel an engine driving engines below it. We have traced the causal, hierarchical chain of order creation from the galactic-scale wheels of astrophysics through the planetary wheels of geophysics, on through the chemical and geochemical micro-scale wheels that drove directly, we argue, the creation of the wheels of life. Of course, not all of this picture is yet certain or sharply defined and many questions remain to be resolved. Most importantly,

perhaps, we cannot yet propose in entirely specific terms testable models for how the final wheels in our story would have arisen and functioned 'abiotically'. But we have suggested a start that could be made experimentally: the initial geological, geochemical and electrochemical conditions are relatively well constrained, the generation of membranes comprising ferrous/ferric sulfides and (oxy)hydroxides well attested [123]. The addition, to the experimental model we have previously investigated, of hydrogen, methane and molybdenum to the alkaline hydrothermal solution, and nitrate to the carbonic ocean simulant, may be enough to put the proposed carbon-fixation and the pyrophosphate engines to trial. These are the engines that would have allowed the free energy sources (the disequilibria) vouchsafed to the planet by the geochemistry of serpentinization operating beneath the Hadean Ocean, to drive, within the chambers of the porous precipitate mounds on the ocean floor, the creation of the specific chemical 'order' which we argue must have arisen for proto-metabolism to have gotten its start—order in the form of disequilibrated states of fixed carbon and pyrophosphate. And, in our view, the goals that must be achieved in this quest now stand before us in relatively sharp focus.

## 11. Epilogue

We began this piece with a quote from Boltzmann from 1886 in which he stated that for 'animate beings' the 'struggle for existence' is not a struggle for energy but 'a struggle for entropy' [1]. Our choice of this quote reflects our view that the point Boltzmann is making is essential to understanding bioenergetics, and not least to how various disequilibria were harnessed at the emergence of life. It is unarguable that what Boltzmann meant by this assertion has long and perfectly passed time's test—a time, moreover, that has seen a great deal of relevant and fundamental progress; for example, the development of non-equilibrium thermodynamics, the understanding of self-organizing dissipative structures, the chemiosmosis revolution and the working out of many of the molecular turnstile mechanisms at the heart of the engines that generate the thermodynamic driving forces of biological systems. However, it seems to us that Boltzmann's assertion about life and entropy, flowing directly as it did from his iconic insight about the physical nature of entropy itself (rightfully regarded as one of the greatest in the history of science) might today, a century and a quarter later, be changed slightly to say that what life struggles for is disequilibrium. For as he well understood and clearly had in mind in his use of the phrase 'a struggle for entropy', life in fact lives by the dissipative consumption of thermodynamic disequilibria and it is through such consumption, suitably enslaved by the intervening operation of organized engines of disequilibrium conversion, that it generates and maintains the exquisitely arranged and complexly connected subordinate disequilibria that make up the necessarily far-from-equilibrium structures and processes that bring matter to life.

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