

Review

# The “Water Problem”(sic), the Illusory Pond and Life’s Submarine Emergence—A Review

Michael J. Russell

Dipartimento di Chimica, Università degli Studi di Torino, via P. Giuria 7, 10125 Turin, Italy; michaelj russell80@gmail.com

**Abstract:** The assumption that there was a “water problem” at the emergence of life—that the Hadean Ocean was simply too wet and salty for life to have emerged in it—is here subjected to geological and experimental reality checks. The “warm little pond” that would take the place of the submarine alkaline vent theory (AVT), as recently extolled in the journal *Nature*, flies in the face of decades of geological, microbiological and evolutionary research and reasoning. To the present author, the evidence refuting the warm little pond scheme is overwhelming given the facts that (i) the early Earth was a water world, (ii) its all-enveloping ocean was never less than 4 km deep, (iii) there were no figurative “Iceland” or “Hawaii”, nor even an “Ontong Java” then because (iv) the solidifying magma ocean beneath was still too mushy to support such salient loadings on the oceanic crust. In place of the supposed warm little pond, we offer a well-protected mineral mound precipitated at a submarine alkaline vent as life’s womb: in place of lipid membranes, we suggest peptides; we replace poisonous cyanide with ammonium and hydrazine; instead of deleterious radiation we have the appropriate life-giving redox and pH disequilibria; and in place of messy chemistry we offer the potential for life’s emergence from the simplest of geochemically available molecules and ions focused at a submarine alkaline vent in the Hadean—specifically within the nano-confined flexible and redox active interlayer walls of the mixed-valent double layer oxyhydroxide mineral, fougérite/green rust comprising much of that mound.

**Keywords:** peptide membrane; fougérite/green rust; Hadean Ocean; hydrazine; mushy mantle; submarine alkaline vents; emergence of life



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*Central to understanding “living mater” is appreciating its sheer improbability. [1].*

*It is through functional properties, not structure, that the organization of a purposive system is expressed. [2].*

## 1. Introduction

The recently revived case for a prebiotic soup in a wet-dry “warm little pond” as life’s womb is—according to a recent article in *Nature* [3]—driven by “scepticism about Russell’s alkaline-vent hypothesis” as it supposedly “lacks experimental support” and moreover, that the “evidence doesn’t exist” [3]. “By contrast, chemical experiments that simulate surface conditions have made the building blocks of nucleic acids, proteins and lipids” [3]. Further, the warm little pond “offers a solution to a long-recognized paradox: that although water is essential for life, it is also destructive to life’s core components” [3]. The further charges variously stated are (1) that prebiotic “molecules wouldn’t survive long in those (alkaline vent) conditions”, (2) that “the formation of these protopeptides is not very compatible with hydrothermal vents” [3], and (3) “None of that synthesis exists in that deep-sea hydrothermal vent hypothesis. It just simply hasn’t been done, and possibly because it can’t be done,” says Catling [3] and, (4) on top of it all Sutherland opines “You can say with some degree of confidence we need to be on the surface, we can’t be deep in the ocean or 10 kilometres down in the crust” . . . “Then we need phosphate, we need iron. A lot of those things are very easily delivered by iron–nickel meteorites” and “once RNA,

proteins and so forth had formed, evolution would have taken over and enabled proto-organisms to find new ways to make these molecules and thus sustain themselves" [4].

In 2017, Sutherland officiated at the submarine AVT requiem in a Nature Reviews, Chemistry paper declaring; "A requirement for ultraviolet irradiation to generate hydrated electrons would rule out deep sea environments. This, along with strong bioenergetic and structural arguments, suggests that the idea that life originated at vents should, like the vents themselves, remain 'In the deep bosom of the ocean buried'" [4]. It appears that to make room in the trend-setting journals for what was assumed by many to be a dead duck, required the peremptory demise of AVT. For example, from these imputations we read "experimental support is growing for the idea that life started in small bodies of water on land" [3]. Furthermore, the case for the "pond" has even earned Catling's blessing: "There's a lot of work that's been done in the last 15 years which would support . . . 'surface lakes and puddles' . . . which are highly promising . . ." [3].

Are they? Here we first argue that the boot is on the other foot; that an ultraviolet UV-energized, wet-dry cycling pond—the alternative Hadean open-womb proposed for life's "origin"—is a reductionist fantasy dreamt up in the absence of geological and thermodynamic consideration. Hence, as this self-referencing pond argument makes its parochial rounds it never finds a home in the biological literature. We will call a variety of witnesses to speak against this "origin of life" pretender and further caution the little pondists of the statistical understanding of thermodynamics, the second law included, known since Boltzmann revealed it to us all back in the eighteen seventies, is fundamental to all dissipative structures in the Universe, and that ignorance of this law is no excuse for endlessly propounding 'origins scenarios that flatly violate it' [5]. We then expose this "false requiem" being played for the submarine alkaline vent theory for life's emergence for what it is, before playing our own overture to emergent life.

## 2. Evaporating Pond Theory of Life's "Origin"

David Deamer has long championed subaerial volcanic hot springs exhaling into shallow ponds subject to evaporation as the birthplace of life. "These wet-dry cycles are everywhere," says Deamer . . . "It's as simple as rainwater evaporating on wet rocks" [3]. "Deamer has conducted several experiments in modern volcanic hot springs to test his ideas. In 2018, his team showed that vesicles could form in hot spring water and even enclose nucleic acids, which Marshall reports "would not form in seawater" [3,6]. "Previously, Deamer and his team in 2008 [7] had mixed nucleotides and lipids with water, then put them through wet-dry cycles. When the lipids formed layers, the nucleotides linked up into RNA-like chains—a reaction that would not happen in water unaided. A follow-up study found that when the resulting vesicles were dried, nucleotides linked up to form RNA-like strands [8]". They conclude, "wet-dry cycles on the edges of the pools would have driven the formation and copying of nucleic acids such as RNA [8]". An "alternate chemiosmotic energy" develops in these supposed conditions though, in contrast to AVT as well as life itself, the gradient is the reverse of the prototypical proton motive force! The disequilibria in their model is provided by reduced sulfur compounds inside the lipid vesicles, the electrons from which are then transported through the membrane by the diffusion of quinone carriers "present in the Murchison meteorite" as they make their way to the ferricyanide acceptor on the outside [6]. As mentioned, protons are also "released in the process, producing an acidic interior and substantial gradients over 2 pH units" [9].

Like Deamer, Frenkel-Pinter and collaborators [10] argue that wet-dry cycles were crucial. "Dry conditions, she says, provided an opportunity for chain molecules such as proteins and RNA to form. But simply making RNA and other molecules is not life. A self-sustaining, dynamic system has to form." Frenkel-Pinter suggests that water's destructiveness could have helped to drive such a system. "Just as prey animals evolved to run faster or secrete toxins to survive predators, the first biological molecules might have evolved to cope with water's chemical attacks—and even to harness its reactivity for good". Moreover, the open ocean is unviable, says Frenkel-Pinter, because there is no way

for chemicals to become concentrated. “That’s really a problem,” agrees Bonfio. The idea is that, with each cycle of wetting, the weaker molecules, or those that could not protect themselves by binding to others, were destroyed. Bonfio and her team demonstrated this in a study this year, in which they attempted to convert simple fatty acids into more-complex lipids resembling those found in modern cell membranes [11]. The researchers created a mixtures of lipids, and found that the simple ones were destroyed by water, while the larger, more complex ones accumulated.” “At some point, you would have enough of these lipids for them to form membranes,” she says. In other words, “there might be a Goldilocks amount of water: not so much that biological molecules are destroyed too quickly, but not so little that nothing changes” [3].

Although wet-dry cycling has been around since at least the nineteen seventies as a proposed prebiotic mechanism for polymerizing amino acids [9,12–14], a similar struggle but with RNA led to the re-opening of Darwin’s casket for the resurrection of “pond theory” [15–32]. However, that casket was empty! In a carefully considered footnote to his Origin of Species of 1872, Darwin wrote “It is no valid objection (to the theory of natural selection) that science as yet throws no light on the far higher problem of the essence or the origin of life” [33,34].

Nevertheless the literature favoring wet-dry cycles is burgeoning. One example is the “polymer fusion model” proposed by Hud and his collaborators [35]. Appealing to retrodiction from the extant RNA molecule—“the penultimate member of a continuous series of polymers”—they suggest that its ultimate precursor was made from primeval prebiotic “hypothetical pre-RNAs”. These “plausible” entities were assumed to exist in the Hadean and were put together from the organic building blocks of life supplied by chondritic meteorites or Miller–Urey prebiotic reactions in a “drying pool” or “drying lagoon”. “My grandfather’s axe” is the pedagogic metaphor called upon to indicate how the ready-made primeval prebiotic “hypothetical pre-RNAs” assumed to exist in the Hadean composed of (1) recognition units (bases), (2) trifunctional connectors (ribose) and (3) an ionized linker (glyoxylate)—the true and pure forebears of RNA and DNA—came to be [35]. But the metaphor, like the scientific assumption contained in the body of their paper, falls short in just invoking the immediate past, for our *palaeo*-grandfather’s axes—unlike grandad’s—were hand-held and made of flint! In opposition we reiterate that the only way to produce biotic monomers and polymers is to start with the simplest of molecules or ions indisputably present on the early Earth, viz., CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, HPO<sub>4</sub><sup>3-</sup>, N<sub>2</sub>, NO, NH<sub>3</sub>, Fe, Ni, Co, Zn, Mn, Mg, Mo, Na, K and reduced sulfur [36–39].

Top-down attempts to mask or muzzle AVT have now been joined by van Kranendonk and colleagues’ [31,32] “bottom up” presentations of geological evidence for AVT’s supposed ‘passing’. The “water problem” is front and center of their argument—a prejudice that harks back to Shapiro’s 1986 isolating assertion: “The enemy is water”! [40]. The van Kranendonk preferred scenario is for a site which has the advantage of “wet-dry cycling and greater chemical complexity (achieved through additional air/volcanic gas-rock, and air/volcanic gas-water interactions, and information exchange between the numerous, chemically variable pools that typify hot spring systems), in addition to the acidic conditions required to form lipid membranes” [31].

To gather support for their preferred model, van Kranendonk et al. [31] explore “deep-time” in search of amenable conditions for their “origin of life”. It so happened that a 3.5 billion-year-old, anoxic hot spring setting from the Pilbara Craton (Australia) revealed “that its hydrothermal veins and compositionally varied pools and springs concentrated all of the essential elements required for prebiotic chemistry (including B, Zn, Mn, and K, in addition to C, H, N, O, P, and S)” [31]. Their argument espouses “temporal variability (seasonal to decadal), together with the known propensity of hot springs for wet-dry cycling and information exchange” and suggests that this “would lead to innovation pools with peaks of fitness for developing molecules” [31]. But this geological scenario falls short of life’s likely onset by nearly a billion years and is no more relevant than other such sites!

### 3. Dirty Chemistry

The struggles to satisfy the RNA world hypothesis in the pond brought about the concept of “dirty chemistry”. This requires a myriad of organic molecules derived from the Earth, atmosphere or extra-terrestrially, to self-organize themselves somehow into the metabolic cycles, thus supposedly explaining how ‘wonderful life’ originated [28,41–44]. Ignored were the earlier entreaties of Schrödinger and Prigogine to understand that, as history itself painfully teaches us, order can only be derived from order, or fluctuations therein [45–47]. Nor is this what we might call “a hypothesis of least astonishment”, i.e., “neither more, nor more onerous causes are to be assumed than are necessary to account for the phenomena” ([48], p. 482).

Dirty, or messy chemistry advocates generally call on lipids as the first requirement to establish a cell. For example, Deamer and Barchfeld studied “how lipids, another class of long-chain molecule, self-organize to form the membranes that surround cells” [3,49]. Deamer and Barchfeld [49] “first made vesicles: spherical blobs with a watery core surrounded by two lipid layers . . . (T)hen . . . dried the vesicles, and the lipids reorganized into a multi-layered structure like a stack of pancakes. Strands of DNA, previously floating in the water, became trapped between the layers. When the researchers added water again, the vesicles reformed—with DNA inside them. This was a step towards a simple cell” [3,49]. Interesting physics and chemistry? Maybe, but it again avoids the problem of DNA’s ultimate source!

Other experiments said to support this heterotrophic origin of life have been made or argued for by Rajamani et al. [7], Monnard et al. [50], Deamer et al. [51], Mulki-djian [52,53], Deamer and Weber [54], Hazen and Sverjensky [55], Kim et al. [56], De Guzman et al. [57], Forsythe et al. [58], Hazen [59] and Pearce et al. [22]. In a similar vein, Powner and collaborators, [16] argue that at “some stage in the origin of life, an informational polymer must have arisen by purely chemical means”. Their publication was particularly impactful, having concluded: “findings suggest that the prebiotic synthesis of activated pyrimidine nucleotides should be viewed as predisposed” (*sic*). In order to demonstrate the verity of this statement, they produced such pyrimidine nucleotides using what they deemed to be “plausible prebiotic feedstock molecules”, viz., cyanamide, cyanoacetylene, glycolaldehyde, glyceraldehyde and orthophosphate. These authors backup the statement with the remark that “the conditions of the synthesis are consistent with potential early-Earth geochemical models.” From the cyanamide, cyanoacetylene, glycolaldehyde, glyceraldehyde and orthophosphate they went on to generate arabinose amino-oxazoline and anhydronucleoside, supposed waystations to the pyrimidine ribonucleotides needed for RNA synthesis! They further remark, “for prebiotic reaction sequences, our results highlight the importance of working with mixed chemical systems in which reactants for a particular reaction step can also control other steps. Although inorganic phosphate is only incorporated into the nucleotides at a late stage of the sequence, its presence from the start is essential as it controls three reactions in the earlier stages by acting as a general acid/base catalyst, a nucleophilic catalyst, a pH buffer and a chemical buffer” on the way to generating “two of the four nucleotides that comprise RNA, starting only with highly concentrated aqueous solutions of phosphate and four simple carbon-based chemicals and cyanamide” [16]. Crucial steps required UV radiation. Thus, they conclude that such reactions could not take place deep in an ocean—only in a small pool or stream exposed to sunlight, where chemicals could be concentrated” [16].

What reactions could these be we ask? Well, UV radiation is normally brought to bear as “a photolysis mechanism that favors selection of the most UV-resistant biopolymers: (e.g., oligonucleotide-like polymers at the expense of the bases) [16] though quite how such substrates are produced in the necessarily exponentially rising concentrations that would be required for such an “origin” of life is not considered. UV has also been heralded as an energy source to free-up an electron from tricyanocuprate  $\text{Cu}(\text{CN})_3$  though again, exactly how the latter is produced in sufficient quantities, or at all, is also not demonstrated [60].

The Earth's volatisphere was simply too oxidized to support a substantial source of that poison [61–63].

In spite of this knowledge, Damer and Deamer [9] suggest that gels might make a good ambient environment for such chemistry requiring, as they do, low water activities. They further report that Sutherland's team [64] "has since shown that the same starter chemicals, if they are treated subtly differently, can also produce precursors to happen in water unaided. Other studies are pointing to different proteins and lipids". They also appeal to cyanide salts—those well-known poisons (pity the poor ferredoxins) where these reactions might have taken place if water containing these salts was "dried out by the Sun, leaving a layer of dry, cyanide-related chemicals that was then heated by, say, geothermal activity". We wait with bated breath to hear of similar 'order-from-disorder' activated chemistry, perhaps to be revealed by NASA/JPL's Perseverance on Mars? But to us all this is wishful thinking dreamed up in an RNA penthouse without solid foundations and no visible means of support in the moderately oxidized and completely flooded surface of the Hadean world. Nevertheless, as this speculation has such a grip on the "origin-of-life" community we give it time of day next.

#### 4. RNA-DNAology

Sutherland's team, using energy from sunlight, has recently produced the building blocks of DNA from high concentrations of photoactivated cyanide (HCN), cyanoacetylene (CH<sub>3</sub>N) and hydrogen sulfide (H<sub>2</sub>S), "something previously thought implausible" [3,65]. Again, no geological evidence for such a soup has ever been mustered. Other suggestions along the same lines call upon prebiotically plausible acrolein and 2-aminooxazol which furnish ribo-3-5P with excellent ribo-selectivity through a combination of kinetic and thermodynamic control.

In a commentary (<https://chemistrycommunity.nature.com> › posts › 3720, accessed on 25 March 2021) on their paper Bonfio and Mansy [66] also inductively conclude that, in the supposed absence (*sic*) of a "historical record", the early Earth's store of electrons required for life resided not in the minerals comprising the Earth *per se* but in a "chemical deposit of NADH" (nicotinamide adenine dinucleotide, C<sub>21</sub>H<sub>27</sub>N<sub>7</sub>O<sub>14</sub>P<sub>2</sub>) (*sic*)! Bonfio and Mansy [66] also relieve origin-of-life theory from the requirement of the early production of the rather complex FMN (flavin mono-nucleotide, C<sub>17</sub>H<sub>21</sub>N<sub>4</sub>O<sub>9</sub>P), suggesting that it too was present in the pond or pool. However, they remarked modestly that they could not be "satisfied" with their model until they had demonstrated that ubiquinone, CoQ<sub>10</sub> (C<sub>59</sub>H<sub>90</sub>O<sub>4</sub>)—a highly hydrophobic molecule—could dissolve in the lipid membrane: which it duly did! This was exciting for Bonfio and Mansy [66] because in biology too, "the electrons donated from NADH to iron-sulfur peptides" are "further transferred to ubiquinone, which is somewhat similar to how electrons pass from NADH to Complex I and then to ubiquinone." Moreover, Bonfio and Mansy [66] suggest that the said electrons were drawn to an even better oxidant than the absent oxygen, *viz.* hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), which, they say "makes sense".

Added to these fortuitous circumstances, according to these same authors, NADH was not the only nucleotide present at that time, because, as it is "generally accepted that RNA and nucleotides were crucial for the origins of life", there must have been a store of them too! They conclude, "the use of electron carriers that fit within the RNA world hypothesis (is) attractive". Bonfio et al. [67] also suggest that UV radiation drives the synthesis of iron-sulfur clusters which are crucial to many proteins. We are told these iron-sulfur clusters would break apart if they were exposed to water, but they were found to be more stable if the clusters were surrounded by simple peptides 3–12 amino acids long. Furthermore, peptides were also apparently to be had, though their source is less clear. However, apparently there was an abundance of lipids available, or generated to order—all of the same length and chirality to provide the first bag for the first cytoplasm! Added to this Bonfio and Mansy [66] opine; "iron-sulfur peptides either engaged in reactions that immediately generated a pH gradient or dumped these electrons on intermediate

polyaromatic electron carriers (which) would have allowed for a simple proto-metabolism to form in a way that was open to further development.” This is the “messy chemistry” idea writ large, and we reiterate our complaint that a plausible prebiotic source of these so-called activated highly-reduced monomers, some of them extremely complex, has not been established and, to our minds, never existed on the early Earth. Moreover, the always present issue of waste disposal—the ‘entropic pull’—is not addressed.

**5. AVT Critiques: The False Requiem**

Here we counterface all the arguments made in recent papers from the very well-funded and promoted groups militantly opposed to AVT [3,68]. One of these papers offers the advice “Don’t try to prove an idea is right. Instead, try to falsify it” [69]. Fully cognizant of Popper’s “Reason and Refutation” [70], this has long been our own mantra, though notably unshared across the community. As an example of good faith, Branscomb and colleagues [71] wrote, “arguably the key virtue of the alkaline hydrothermal vent (AHV) model as a scientific hypothesis regarding the initial steps in the emergence of life is its essentially unique vulnerability to disproof. It places all of its chips on the claim that certain naturally arising, but experimentally reproducible, geochemical circumstances do produce castles of mineral ‘cells’ in which three key, undeniably life-like chemical disequilibria are ‘abiotically’ generated and maintained. If it proves not to be possible to experimentally substantiate these conjectures, then we may expect interest in the theory to wane.” Furthermore, falsifiable predictions of AVT were listed in Russell [72] that would, if demonstrated, “reveal embarrassing missing links, or even leave the AVT as just one more casualty of the general theory of natural rejection.” We look forward to similar commitment and clarity from the wet-dry polymerizing pond people. However, we do admit to being impressed over the one prediction made by this group—viz., Dimitar Sasselov’s promise that Harvard University “will soon have the equivalent of a living thing in the lab at the chemical level”. We will be particularly interested to hear what bearing such an artifact might have on the putative ‘first universal ancestor’, its evolving progeny and the geochemical/geophysical disequilibria responsible for its emergence [68]?

One prejudice held against AVT is owed to the denial of known Hadean conditions by those who would attempt, as mentioned, the resuscitation of Darwin’s off-the-cuff remark in a letter to Joseph Hooker, now known in Tabloid speak as “Darwin’s warm little pond” [73]. In contrast, the AVT is built solidly in acknowledgement of the geological, geochemical and geophysical conditions on the early Earth as assembled by countless scientists. The retrodicted mineralogy of the early Earth cannot be dismissed merely by writing “it is uncertain whether these (minerals) were available on the prebiotic Earth” [74]. To counter this statement, we present in Table 1 all the evidence pertaining to our contention that the rocky surface of the Earth was always submerged in the roiling Hadean Ocean. Indeed, we challenge those that would favor the putrid pond idea to counter all these aspects of the Hadean Earth listed in Table 1—a world so different than today’s that it is wiser to think of it as a different planet.

**Table 1.** A Hadean Advisory.

Effects	Descriptions	References
Solar luminosity post solar wind	72% of present flux	[75]
Solar radiation (UV and X-ray)	Intense: ~100 + times present <10% of present day;	[76,77]
Earth–Moon distance; Earth’s spin and length of day and tides	Estimates of length of day from 2 to 10 h; ~20 m tidal amplitude	[78–91]

Table 1. Cont.

Effects	Descriptions	References
Bombardment and tsunamis	Heavy but not totally vaporizing (negative feedback from heightening atmospheric pressure)	[92–97]
Maximum height of ocean plateaux above by mantle plumes.	~1000 km	[98–107]
Ocean depth	4–6 km	[108–117]
Redox state	Upper mantle buffered at quartz-fayalite-magnetite	[62,63,118–120]
Atmosphere post solar wind	CO <sub>2</sub> , N <sub>2</sub> , H <sub>2</sub> O, > SO <sub>2</sub> >> CO, NO <sub>x</sub>	[121–133]
Ocean chemistry	Saline, CO <sub>2</sub> , NO <sub>3</sub> <sup>−</sup> , NO <sub>2</sub> <sup>−</sup> + metal ions	[134–140]
Magma-driven submarine springs	Acidic, ~400 °C	[141]
Direct contribution of ~400 °C solution to Hadean Ocean	Fe <sup>2+</sup> , Mg <sup>2+</sup> , Mn <sup>2+</sup> , Zn <sup>2+</sup> , Co <sup>2+</sup> , Ni <sup>2+</sup> , H <sub>2</sub> S, H <sub>2</sub> , PO <sub>4</sub> <sup>−</sup> , CH <sub>4</sub>	[142]
Serpentinization-driven submarine springs	Alkaline, ~120 °C	[143–147]
Direct contribution of ~120 °C alkaline spring to the hydrothermal mound	H <sub>2</sub> , CH <sub>4</sub> , HS <sup>−</sup> , HCOO <sup>−</sup> > [Fe <sub>2</sub> S <sub>2</sub> (MoS <sub>4</sub> ) <sub>2</sub> ] <sup>2−/4−</sup>	[142–149]
Ocean T & pH and chemistry	Strongly carbonic and saline 25 to <85 °C? pH 4.5 to 5.5 with minor nitrate, transition metals in solution fed from ~400 °C springs	[129,141,150–155]
The Earth electronic and protonic ~1 volt battery	Eh of H <sub>2</sub> v. H <sub>2</sub> O at delta pH 4 to 5	[136,156–159]
Olivine source of pyrophosphate delivered to ocean via vulcanism	Hydrolysis of volcanic P <sub>4</sub> O <sub>10</sub> to produce P <sub>3</sub> O <sub>9</sub> <sup>3−</sup> and P <sub>4</sub> O <sub>12</sub> <sup>4−</sup>	[160–162]
Lightning	Produces NO from CO <sub>2</sub> + N <sub>2</sub>	[131,163–169]
Wind speed (cf. “Roaring Forties”)	12 ms <sup>−1</sup> estimate	[170]
Wave height	10 m estimate	[86,170]
Chemical sediments	Banded iron formation, fougurite, chert, greenalite, mackinawite	[171–179]

Foremost amongst Damer and Deamer’s [9] various objections to submarine alkaline hot springs also depends on that so-called “water problem”. For example, they argue that, “as a general rule, the much higher concentrations of ionic solutes composing seawater inhibit self-assembly of membranous structures and encapsulation of polymers.” Furthermore that, “the water activity within a submerged mineral cavity . . . will be at equilibrium with the surrounding ocean bulk.” “This presents a significant thermodynamic hurdle because in aqueous solutions condensation reactions leading to polymer synthesis would require chemically activated monomers such as the nucleoside triphosphates that drive biological metabolism or the imidazole esters of mononucleotides used in the laboratory.” They continue, “a plausible prebiotic source of activated monomers has not been established experimentally.” However, as has long been known, there is no reaction-driving free energy in a single phosphate-reactant bond! The free energy is in the displacement from equilibrium of the pyrophosphate/phosphate-ratio. Still Damer and Deamer go on, “due to the aforementioned water problem, should any catasanalytic polymer, let alone one so complex as a primitive ATP synthase, be formed by chance in a vent environment, without the constant repair and resynthesis by the enzymes of biology, it would soon be disassembled by hydrolytic decomposition.” (Given the problem of “constant repair and resynthesis”,

we wonder how the process of repair would be managed as life was supposedly ‘birthing’ in an evaporating pool?) They add, “cycling of systems of polymers . . . that can drive molecular evolution along the path to cellular life . . . is not available in a continuously immersed environment.” Moreover, such “sites are compromised because of the uniform, dilute nature of the ocean reservoir and its limited capacity to concentrate either the simple organic compounds or the trace elements required for prebiotic chemistry” [9].

Damer and Deamer’s complaints are echoed, as we have noted, by Frenkel-Pinter and Bonfio [3], and have also been reiterated by Voosen [180]. Van Kranendonk et al. [31] take up the same cry, calling upon Mulkiđjanian et al. [17], Hud et al. [35] Ross and Deamer [20] and Deamer et al. [51] for support when they write “Oceans are also considered unlikely sites for OoL due to their limited capacity for complexity, the high salt and total divalent cation (e.g.,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) concentrations that inhibit lipid membrane assembly and protocell formation, and because organic polymer formation requires condensation reactions at sites where wet–dry cycling can take place (“The Water Problem”).” However, this lipid argument has no phylogenetic support nor any bearing on the submarine alkaline vent theory.

In AVT, the first membranes comprise, for example, multilayered enantiomeric 16-mer residues such as Ala-Glu-Ala-Glu-Ala-Lys-Ala-Lys amyloid beta-sheet peptides [181]. Moreover, Ser-Gly-Ala-Gly-Lys-Thr-alpha sheets that we also favor are so much more functional, even as information molecules [163,181–185]. These peptides can also act as alpha-helix P-loops [181,186–192]. Therefore, the Damer–Deamer complaint regarding the supposed problem of encapsulation does not apply to peptide membranes which are known to precipitate in such environments [9,191,192]. Surely, the assertion that condensation reactions (or catalysis in general) cannot take place in water could be read to assume life’s wet cells are also unviable! The nanochemistry and nanotechnology literature appears to have passed these complainants by! In AVT’s defense redox catalysis and polymerization can be promoted within nanometer-sized pores and interlayers such as to be found in layered double hydroxides, including fougurite (~green rust), silica films, amyloid and peptide nests [72,193–216]. Moreover, it should be recalled that the AVT is the only theory which proposes a viable and explicit mechanism for the generation of out-of-equilibrium pyrophosphates as we will address in the next section.

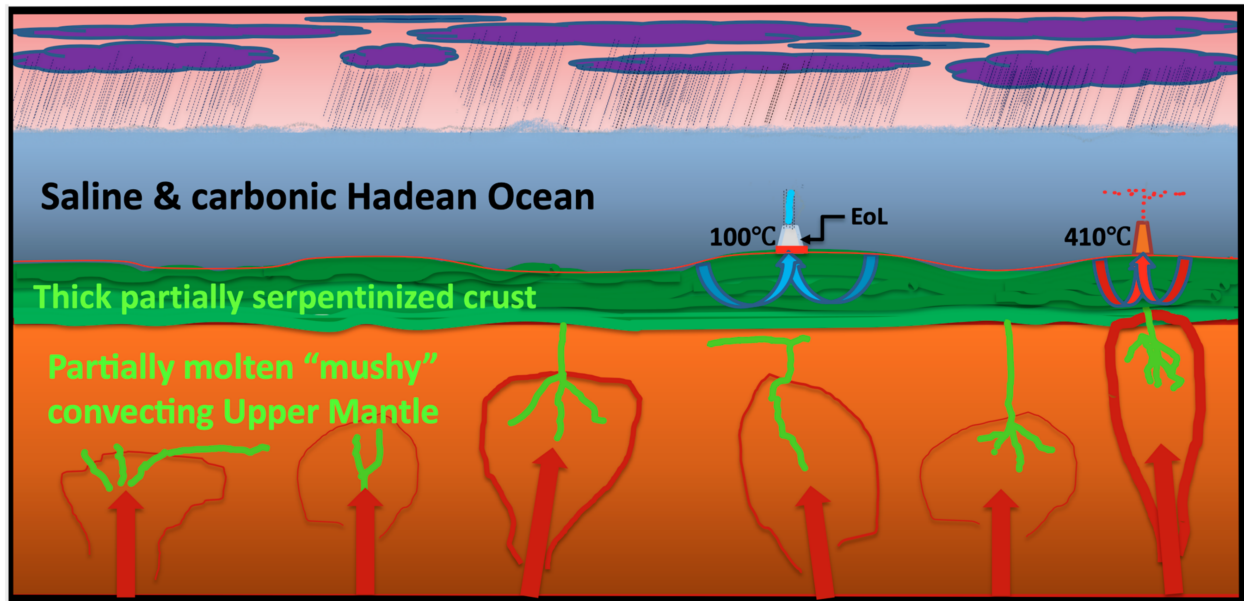
Damer and Deamer [9] exclaim that “the experimental evidence and thermodynamic models of the vent hypothesis have recently been challenged and these critiques should (also) be addressed [9]. This seems particularly egregious; the facts are that the Jackson “criticism” [217,218] had already been thoroughly rebutted by Lane [219]; the explanation for how life left the vent environment was previously detailed in Russell and Hall [156,159], and the Ross [220] criticism has been exhaustively excoriated by Branscomb and Russell [221] without rejoinder. Wächtershäuser’s [222] challenges apply to the pond theories more than they do to the AVT and we deal with them in their own right in the next section. But first we can report on their reasonable challenge [9] that “one such test . . . for the vent scenario is that carbon dioxide can be reduced to simple organic solutes such as formic acid in a vent environment” [223,224]. Such a test has now been experimentally demonstrated both in the serpentinizing system and the vent environment [143,225].

A further directive is that “(H)ypotheses for an origin of life must also propose that a cell-sized compartment is able to maintain sufficient concentrations of reactants so that metabolic reactions can be initiated.” This challenge has also been met both theoretically [226,227], as with recognition that “surface area available for catalytic processes exceeds that of a solid crystal by orders of magnitude”, and in experiments that show the product exceeds that to be expected of the mere surface of green rust/fougurite [227–232], products that include ammonium, amino acids and, perhaps, hydrazine [185].

While it is admitted by Damer and Deamer [9] that the Hadean Earth did not have continents, they do argue that it was likely to have volcanoes similar to those from the same era still visible on Mars. Volcanoes yes, tens of thousands of them probably, but given the mushy state of the mantle [98] and ergo its limited load-bearing capacity, the salience of



plume-related large igneous provinces and the tumultuous weather of the era, then the idea of Hadean volcanoes hosting fresh water ponds is, in Wächtershäuser's terminology, a "pre-falsified" theory" one "that falls stillborn off the press" [222] (Table 1, Figure 1). Further, the view that the "concentrating potential" of reactants, e.g., "amphiphilic compounds", in such a pond adds significant free energy to a system that can be used to drive condensation reactions flies in the face of how entropy is reduced in general [47], let alone how these putative reactants would be produced in the exponentially increasing concentrations required by life's procreation and evolution!



**Figure 1.** Depiction of our Hadean planet. The crust was completely submerged with a ~5 km deep ocean as the magma ocean was still too mushy to support significant bulges even at the apices of mantle plumes [98–102,106,233–235] EoL: emergence of life.

It seems to have escaped our critics that the AVT is not an "origin" story but a theory of "emergence" of a unique dissipative structure [1,226] because "organismic wholes cannot be built piecemeal from molecular parts, and the "whole provides rules and contexts in which parts emerge and acquire functional significance" [1]. The RNA world's opposition to the AVT is still argued despite (because of?) the several cogent refutations of the RNA world by and repudiations of soup theory [236–244]. These objections to the wet/dry RNA pond models have been comprehensively ignored and remain to be answered. It seems there is more to be had by challenging the counter theory—the AVT—rather than facing up to the proverbial mote in the eye.

In the Damer–Deamer [9] critique we further read not only that the AVT could not survive the dilution (of organic molecules) that inevitably would occur in a global salty ocean, but also that "seawater is too salty" to let lipids come together to form membranes and threatening the stability of any of those that threaten the stability of lipid membranes. However, to counter this view, Jordan and his coworkers [245] have demonstrated the viability of lipids to do just that, though they do not specify a lipid source. Damer and Deamer [9] carry on with the suggestion that the cycling of systems of polymers through distinctive dry, wet, and moist phases will drive molecular evolution along the path to cellular life, "a process that is not available in a continuously immersed environment".

It is noteworthy here to emphasize that, notwithstanding the text book diagrams showing lipids to dominate the cell membrane, they barely constitute 20 to 30% of these structures; that role is mainly taken by the proteins. Their remark is also irrelevant to AVT anyway as the lipids in archaea and bacteria have opposite chirality and the split is likely to have been after the last universal common ancestor (LUCA) [246–249]! Nevertheless,

we read that “submarine hydrothermal vents represent a later adaptation for extremophilic microbial life that can thrive in conditions vastly different from the clement pools where life can begin” [9]. This tempts us to ask the same question put by the poet in the biblical book of Job, “Have you descended to the springs of the sea or walked in the unfathomable deep . . . Have you comprehended the vast expanse of the world?” ([250], p. 192).

## 6. Wächtershäuser’s Probe

In contrast to the rather loose criticisms of the little pond people, Wächtershäuser’s are quite precise [222]. For example, he writes, the “ingenious FeS-membrane theory (Russell et al. 1989 [36]; Russell and Hall 1997 [157]) postulates an open cell structure within a precipitated mound of FeS at the bottom of the primitive ocean” but then charges that the microphotograph used to demonstrate such structure was in reality an artifact of freeze-drying. This is as maybe, but more recent experiments that also consider green rust precipitation, belie this charge [232]. A further criticism, that concerning the supposed instabilities in a hydrothermal mound, is grounded in the assumption that any organic polymers produced there are unstable. Yes, they would be if it weren’t for the fact that water activities would be so low in the nanoconfined spaces in fougérite/green rust and within the subsequent peptide nests as to possibly promote condensation reactions, while there would still be water enough for necessary hydrolyses to proceed in that same environment [72,201,251].

With respect to mineral membranes in general [252,253] Wächtershäuser [222] also doubts that they could hold a pH gradient sufficient to drive, for example, phosphate condensation in an approximation of the proton motive force as well as a delta Eh sufficient to drive other protometabolic processes. Our expectation was that orthophosphate driven into green rust interlayers would, as in pyrophosphatase, condense to pyrophosphate in the conditions obtaining at the alkaline vent [72,100,123]. To the former challenge Qingpu Wang and his coworkers [254] have recently demonstrated just such a condensation of ortho- to pyrophosphate in a microfluidic device driven by a delta pH of 3.6. Nevertheless, we readily admit that other biology-like condensations await further experimental testing and demonstration [255]. The remainder of Wächtershäuser’s [222] criticisms make much of Hadean conditions which are more directed to the RNA world proponents and anyway are dealt with in some detail below. However, still missing from Wächtershäuser’s [222] diatribe is a status report on his own “pyrite hypothesis” for the “origin of life” [256].

## 7. The “Pond” in the Hellish Hadean

*Pace, Sleep and collaborators’ [257] and Damer and Deamer’s [9] opinions, there were no “clement surfaces”, or “clement pools” to be had on the surface of our Hadean planet—that young water world, impacted as it was by high energy UV, X-rays, meteorites and asteroids, was no place to conceive and succor life. On the contrary, that young world was spinning at such a rate—a day likely lasted less than 8 h—and the moon was so close as to engender perpetual hurricanes, endlessly roaring 10 m high storm waves and rapid tidal oscillations in an ocean with twice the present volume [108–117]. However, we read in Damer and Deamer [9] that volcanoes “emerging through a global ocean would be the original land masses on the Hadean Earth analogous to Hawaii and Iceland” with “abundant hydrothermal fields with multiple hot spring systems replenished by precipitation evaporating from the surrounding ocean. The distilled fresh water would percolate into hot rocks and then circulate back to the surface as springs and geysers. Hydrothermal fields provide sources of heat and chemical energy to drive polymerization reactions in films of concentrated organic solutes that form on mineral surfaces during repeated cycles of wetting and drying.”*

Travelling back to when the Universe was only two thirds its present age we would be observing a very different planet where surface conditions were unrelentingly tumultuous; the likely depth of the Hadean Ocean was about 5 km; and the mushiness of the upper mantle could not support notional ‘Iceland’ or ‘Hawaii’, with their supposed tidal pools,

ponds or land-locked seas as sites for the origin of life [98–117]. Even so Carrell opines that a “larger ocean exacerbates the biggest strike against the underwater scenario: that the ocean itself would have diluted any nascent biomolecules to insignificance.” [180]. No mention is made of the autogenic emergence of life favored by scholars of early metabolism and as assumed in the submarine AVT—that is through the generation of organic molecules from the simplest of carbon-bearing precursors from the bottom up, in the hydrothermal mound precipitated at the alkaline vent [36,38,39,72,166,185,223–227,239,240,247,248].

That the earth’s atmosphere has been mildly oxidized and oxidizing over the last 4.4 Ga is because the redox state of carbon in the quartz-feldspar-magnetite buffered hot upper mantle is as carbonate. This seems surprising given that the Earth is largely an amalgam of metal-bearing chondrites, many of them carbonaceous. The reasoning goes that as the olivine-rich mantle is subjected to pressures beyond ~21 GPa in the lower mantle, it tends to metamorphose to perovskite, a mineral that requires a 3<sup>+</sup> valence metal, normally aluminum. However, as the concentrations of Al<sup>3+</sup> in the mantle are too low to meet this entire need, iron in the olivine disproportionates, with Fe<sup>3+</sup> deputizing for the lacking Al<sup>3+</sup>, while the native iron Fe<sup>0</sup> tends to gravitate to the core [61–63,85]. The result is a relatively oxidized volatisphere comprising CO<sub>2</sub> > H<sub>2</sub>O >> N<sub>2</sub> [85,124–139].

### 8. The Retreat to Mars!

Some of the proponents of the ‘RNA-world hypothesis’ who recognize the geological, geophysical, isotopic and magmatic evidence for the early Earth being a “water world”, have retreated to Mars for their favored subaerial intermontane valleys assumed to have sheltered lakes subjected to wet-dry cycling [18,258–261]. According to this view, such valleys would have received high pH run-off from a watershed rich in serpentinizing olivines and eroding borate minerals in which to cosset and cook their organic soups. As water evaporated, “nucleobases, formylated nucleobases, and formylated carbohydrates, including formylated ribose, can form”(sic). We are then assured that “well-known chemistry transforms these structures into nucleosides, nucleotides, and partially formylated oligomeric RNA” [18]. Life that so emerged there was then distributed through a local panspermia to the otherwise deserted oceans of the early Earth. To our mind, this is the one speculative example where water would have been the enemy!

This whole idea of panspermia as an explanation for the “origin” of life on Earth was first given credence by no less than Hermann von Helmholtz in 1871 [262]—a suggestion provoking this scolding (in absentia!) from Karl Marx in 1875 [263]: “Helmholtz disseminated the absurd doctrine that the germs of terrestrial life fall ready-made from the moon, i.e., that they were brought down here by aerolites. I detest the kind of explanation which solves a problem by consigning it to some other locality”.

### 9. Experimental Results Pertinent to the AVT

How is the AVT faring in the face of Sutherland’s [4] assumption that a “requirement for ultraviolet irradiation to generate hydrated electrons would rule out deep sea environments”? He continues “This, along with strong bioenergetic and structural arguments, suggests that the idea that life originated at vents should, like the vents themselves, remain ‘in the deep bosom of the ocean buried.’” We disposed of this fallacy in Section 2, and subject it to thermodynamic interrogation in Section 7. In Table 2, we list the experiments that have been applied to the AVT and their various outcomes since its first airing [36]. The AVT was not a passing whim to appear fully formed as that “pond” did in one of Darwin’s unguarded musings in that letter to Hooker. It had its own testing from its accidental conception, through a 30 year period of gestation beginning with employment in the chemical industry, although the actual form it took on its delivery in 1989 could not have been guessed (Table 2) [36,264]. The basis of submarine AVT is that the environment can support the continuous synthesis of large populations of monomers, encapsulating them in compartments which permit the formation of polymers of catalytic length. The current experimental focus of the submarine alkaline hydrothermal vent theory is to utilize free

energy gradients for the synthesis and metabolic engagement of small organic molecules and monomers, which are precursors to biochemical processes. Further, the necessary disposal of waste is taken care of by direct hydrothermal expulsion in the ocean [5,47,72].

So, what are the AVT's successes? To reiterate Russell [72]: the AHV theory did effectively predict the presence of off-ridge alkaline vents in the present oceans, a prognosis met by the discovery of the Lost City submarine alkaline vents in 2000 [36,146,265]. It also explains, for example, why early life did not have to invent such a counterintuitive mechanism as that entailed in Mitchell's proton motive force to drive phosphate condensation (the only theory so to do) [142,266], how it was supplied with the necessary low entropy C1 feed [36,162,267], how biosynthesis could proceed in a highly radiated and mildly oxidized atmosphere [119], and why it was not destroyed by surface catastrophes in the Hadean" [95]. Since then, a microfluidics experiment by Hudson et al. [225] has demonstrated the reduction of CO<sub>2</sub> to formate in a pH gradient, a key prediction of AVT. However, a natural proton motive force does not appear to have been the driver, and such a demonstration remains to be realized. We summarize other experimental results to be expected of the AVT in Table 2.

**Table 2.** An AVT status report.

Prediction/Expectation	References	Tests	References
Hydrothermal circulation during rift tectonics generates metal sulfide mineral deposits. Seawater-derived	[268]	Successful field test, discovery of giant base metal deposit, Navan, Ireland	[269,270]
Downward hydrothermal convection driven by crustal heat and exothermic reactions	[271–274]	Stratigraphic, structural, tectonic and lithochemical field work; Lead isotope analyses	[275–277]
Some hydrothermal minerals precipitate on sea-floor	[269–273]	Delineation of extensive Mn aureole centered on Irish ore deposit led to the first discovery of fossil hydrothermal chimneys formed through mixing with seawater	[277–282]
Some sulfur derived from crustal sources	[157,273,283]	Isotopic analysis reveals crustal source as do hydrothermal experiments	[196,197,276]
Sulfide dissolves in alkaline hydrothermal solution	[157]	Lab demonstrations	[196,197,225]
Serpentinization reaction to formate	[284–291]	Lab demonstration	[226]
Serpentinization reaction produces H <sub>2</sub> >>CH <sub>4</sub> , although CH <sub>4</sub> is entrained from oceanic crust	[292]	Prompts amendment to the AVT, viz., to the denitrifying methanotrophic acetogenesis	[267]
Lightning and space weather radiation produces NO <sub>x</sub> that rapidly dissolve as nitrate/nitrite in Hadean Ocean	[126]	Theoretic studies generally support this hypothesis though not those of Ranjan et al. 2019 [286]	[131]
Source of ammonia at vent from nitrate/nitrite reduction	[126,163]	Eight electron reduction of nitrate to ammonia with green rust	[193,194,230]

Table 2. Cont.

Prediction/Expectation	References	Tests	References
Further reduction of NO <sub>x</sub> to hydrazine N <sub>2</sub> H <sub>4</sub>	[80]	Awaiting test	
Off-ridge submarine vents will be moderate temperature, H <sub>2</sub> -bearing, alkaline and long-lived ( $\geq 10^5$ years) and would have been the site of life's emergence	[36,136,157,264,293]	Discovery of Lost City moderate temperature alkaline hydrothermal vent in North Atlantic Ocean	[146,265]
Green rust, mackinawite/greigite, amorphous silica barrier/ membrane Eh and pH gradients	[36,39,72,294]	Successful lab demonstration	[36,159,197,232,251,295]
~700 mV and 4–5 units pH (~300 mV) to meet electronic and protonic requirements ~1 V	[157]	FeS barriers hold a 700 mV and a 5 unit pH disequilibrium in lab test	[199,231,254]
CO <sub>2</sub> reduction forced by H <sub>2</sub> and delta pH 4 units	[157]	Chemical disequilibria as per Nernst equation	[226]
The immateriality of the “water problem” in nano-confinement	[72,296–305]	Lab and molecular dynamic simulations	[201,202]
Aminations of carboxylic acids	[72]	Lab demonstrations. Amination of pyruvate to alanine	[231]
Green rust as proto-pyrophosphatase	[228]	Pi + Pi → PPi to equilibrium in microfluidic reactor	[254]
$\Delta pH$ as <i>pmf</i>	[63,156,157]	Undemonstrated	
Oxidation of methane in green rust	[72,267,306]	Undemonstrated, pending	Cf. [307]
Theoretical polymerization of amino acids in nano-confined water to produce peptide membranes necessarily pre-LUCA	[72]	Undemonstrated, waiting experiment	
Expansion from the vent via ocean floor to produce the first deep biosphere	[156]	Hypothesis	

## 10. How Might the Nucleotide Penthouse be Accessed from the Submarine Alkaline Vent

In a masterly critique of an article by Avshalom Elitzur [308], Yockey [34] muses on why the “primordial soup” hasn’t yielded the RNA world. This search, he suggests “seems to have been left for later in the manner of an ingenious architect in the Grand Academy of Lagado, as reported by Captain Lemuel Gulliver in Jonathan Swift’s Gulliver’s Travels. This architect contrived a new method for building houses by starting at the roof and working down and establishing the foundation at the end of the project. The architect pointed out that among the obvious advantages of this method is that once the roof was in place the workers could toil in the shade of the hot sun and at other times be protected from rain and snow. Thus, the progress of the construction would not be delayed by inclement weather. Although this idea had been approved by peer review, it was still in the research stage and he had not yet put in into practice at the time of Captain Gulliver’s visit.” Yockey continues; “following the reasoning of the architect in the Grand Academy of Lagado, cites the existence of life as a justification and a proof that a primeval soup must have existed.”

Further, “the model proposed (of the origin of life) here is based on a simple assumption, namely, that life began with the accidental assembly of a self-replicating molecule (in a primeval soup). From this assumption the emergence of life naturally follows, enabling a new understanding of evolution as a whole. Thus, Elitzur and others are not deterred in their beliefs by the fact that the absence of evidence is indeed evidence of absence” [34].

All the geological and geochemical evidence demonstrates that the RNA world’s required ingredients for the Damer–Deamer soup; lipids, HCN, CH<sub>3</sub>N, H<sub>2</sub>S, H<sub>2</sub>O<sub>2</sub>, quinones, ferricyanide soup [9] simply weren’t available, and those sought by Bonfio and Mansy [66] such as acrolein, 2-aminooxazol, RNA, DNA, NADH and FMN, were even more outlandish. However, could the “submarine geyser help”? Duval and collaborators [185] point out that condensation of two amino or azanyl radicals will produce hydrazine in the interlayers of a hydrotalcite such as green rust. Hydrazine is an excellent feedstock for production of pyrazoles and imidazoles and other heterocyclic compounds—staging molecules for the nucleobases and the organic enzymes [185].

With this in mind, we compare and contrast the pond theory with the AVT in terms of putatively available “free energies” in Table 3.

**Table 3.** Pond and AVT chemistry and “free energies” compared.

	Surface Pond	References	Submarine Alkaline Vent	References
“Free energy”	UV, reverse 2 pH unit pmf	[7,16,59,60,68]	Electrochemical gradients, natural 4 pH unit pmf	[156,157,199,219,226,231,254,291]
Electron donors	UV radiation, reduced sulfur & organic compounds, Fe <sup>2+</sup>	[3,10,30,65]	Fe <sup>2+</sup> , H <sub>2</sub> , e <sup>-</sup> , CH <sub>4</sub> , HCOO <sup>-</sup>	[5,36,39,63,72,156,157,247,248,267,284,291,306,309,310]
Electron acceptors	Ferricyanide inside vesicle	[9]	Ambient Fe <sup>3+</sup> , NO, NO <sub>2</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> (CO <sub>2</sub> )	[39,131,157,166,291]
Initial boundary	Lipids	[7,49,51,64]	Green rust, FeS, silica	[36–39,72,157,291]
Organic takeover	Lipids	[7,9]	Peptides	[181,184,185,190–192,215,216,237,311]
Primary ingredients	Lipids HCN, CH <sub>3</sub> N, H <sub>2</sub> S, H <sub>2</sub> O <sub>2</sub> , quinones, ferricyanide	[9]	CO <sub>2</sub> , H <sub>2</sub> , CH <sub>4</sub> , H <sub>2</sub> O, NO <sub>3</sub> , NO, NH <sub>2</sub> , NH <sub>3</sub> , HPO <sub>4</sub> <sup>3-</sup> , HS <sup>-</sup> , Fe <sup>2+</sup> , Ni <sup>2+</sup> , Co <sup>2+</sup> , Mo <sup>4+/6+</sup>	[116,129–138,143,196,197,225,291,312]
Other suggestions orderivatives	Acrolein, 2-aminooxazol, quinones, ferricyanide, RNA, DNA, NADH, FMN	[11,16,30,60,64–67]	NH <sub>3</sub> + carboxylic acids → amino acids, N <sub>2</sub> H <sub>4</sub> → heterocycles, e.g., pyrazoles, imides, NAD(P), flavins, quinones	[185,193,194,230,310]
Disequilibria conversion mechanisms	Wet/dry cycling aggregation	[7]	Visco-elastic allosteric conformational changes/binding change mechanism/pumping/gating/electrostatic effects	[5,47,71,72,181–192,221,228,310,313–324]
Condensations	Wet/dry cycling	[9,20,21,24,57]	Nanoconfined water in green rust interlayers, silica, mackinawite	[72,80,88–90,96,97,100–104,123,125,302]
Reproduction	RNA world	[9,17,22,51,64]	Amyloid peptide	[72,211–216,325,326]
Waste disposal	None considered	—	In alkaline spring effluent	[36,47,72]

## 11. The “Origin of Life” Community

One of the inhibiting factors for the “origin of life” community is a general reluctance to accept that the emergence of life is a transdisciplinary, *hard* problem. Thereby, there is a tendency to ignore research disciplines outside of the main interests of the researchers

themselves. Two significant disciplines that most researchers have an aversion to are those of geology and statistical thermodynamics. In this contribution, we have attempted to explain the geologic conditions at, and for, life's emergence. For Boltzmannian thermodynamics as it applies to the AVT, and how pond theorists have failed to come to terms with it, the reader is referred to references [5,47,71,221,228].

## 12. What's Next for the AVT?

None of the above criticisms of pond theory in this polemic should be taken to imply that the AVT has no serious issues or research challenges of its own. First amongst these is whether partially sulfurized green rust/fougerite was literally the first seed of life—exploited by the local disequilibria as a 'makeshift' protocell to enable their dissipation [72]—or was it merely coopted by peptides generated in the same environment along with iron sulfide—synthesized on site to be exploited as the first multi-tasking proto-enzyme, (or, of course, was it involved at all) [185]? Either way, many of the research challenges for the hypothesized role(s) of fougerite—dosed with various trace elements and anions—are similar. Such research addressing the submarine acid v. alkaline milieu calls for the further employment of tried-and-tested microfluidic and nano-crystallographic techniques [192,201–207,224,254,296–302,310,327–338]. We enumerate some possible developments from, expectations of, and tests for, the AVT below:

1. Can the fougerite/green rust interlayers—already shown to effect the relatively rapid eight electron reduction of nitrate to ammonia through-edge inward oxidation—be recharged from electrons generated at a transition-metal-rich hydrothermal vent (acting as a hydrogenase) through iron-to-iron hopping along the green rust metal oxide layers; i.e., is the green rust battery rechargeable at the vent [72,158,199,324,328,336–339]?

2. While green rust has been shown to be capable of aminating carboxylic to amino acids [231,340], the next vital and major challenge for the AVT is for a demonstration of condensations of amino acids to short peptides.

3. Could an NO intermediate, produced from nitrite at Fe sites within the interlayers of fougerite, oxidize methane to a methyl group [267,306] cf. methane monooxygenase and the  $\alpha$ -Fe/ $\alpha$ -O active site in Fe-CHA zeolite [307]?

4. What proportion of the chemical transformations produced within green rust interlayers is the result of electrostatic forces and what is due to directional stresses and, anyway, are the two coupled [71,72,314,321–323]?

5. Further, are there analogies to be had, for example, between the electrostatic and conformational changes during polaron migration within the green rust interlayers to be expected during continuous reductions of nitrate and nitrite, with the changing dimensions of the Fe-N site in nitrite reductase [193,194,230,324,338,341]?

6. Do  $\text{Fe}^{3+}$  polarons in general act to pump anions nano-peristaltically into and/or through the green rust interlayers, as well as pump nutrients through, and toxins and uncooperative molecular waste out of, the system [6,72,315–318,324,338]?

7. In the same vein, can low pH (local acidity) drive the condensation of orthophosphate to pyrophosphate to high disequilibria at the edges (binding sites) of fougerite galleries where the entropic state and water activity are low in the manner to be expected of the core of bioenergetics [310]? If so, can immediate hydrolyses leverage trapping of condensation reactions at neighboring (and oscillating) binding sites (cf. certain pyrophosphatases), i.e., can 'macromolecular' green rust effect alternating independent coupling as in the binding change mechanisms that are known to operate in enzymes such as the proton pyrophosphatases [72,228,315–318]?

8. Would a similar process result in the condensation of  $\text{NH}_2$  radicals to  $(\text{N}_2\text{H}_4)$  hydrazine, a step to heterocyclic redox molecules and the nucleotide world [185]?

9. Can the putative escapement mechanisms and information ratchets in the first green rust/fougerite nanoengines of life referred to above, work to produce the asymmetry and the irreversibility in a system necessary for life's emergence—it's climbing the steps that's hard [2,6,72,318–323]?

10. In AVT, information transfer would have emerged coupled to protometabolism “in materio” in the green rust/fougerite interlayers: a fertile research area that begins to converge with research in emergence of intrinsic computing, nanoscience and nanotechnology [1,34,215,216,311,334,342–360].

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