Introduction


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The origin of life: the submarine alkaline vent theory at 30

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Everything new is on the rim of our view, in the darkness, below the horizon, so that nothing new is visible but in the light of what we know.

—Zia Haider Rahman

The emergence of life is, to borrow from Churchill, a riddle, wrapped in a mystery, inside an enigma. But little by little we are unwrapping it. The submarine alkaline vent theory (SAVT) for the emergence of life, now 30 years old, has reached the stage where it provides a clear path forward in experimentally testable hypotheses that involve a transdisciplinary approach to the issue. These papers record a meeting from the 11th to 15th March 2019 in Granada, Spain, to celebrate the 30th anniversary of the alkaline vent theory of the origin of life (figure 1). This issue contains selected contributions from that meeting that provide both new theory as well as experimental and computational evidence to indicate the progress of the SAVT made since its inception. Much of the first 30 years has been given to detailing the initial geological, geophysical and geochemical conditions that forced life into being, and experimental testing of many of the underlying geochemical assumptions. The work included attempts to build plausible anaerobic autotrophic pathways toward the roots of the evolutionary tree—a tree that ‘broke ground’ as LUCA, the last universal common ancestor. The protometabolic pathways—given to the hydrogenation of atmospheric carbon dioxide—were thought to have been guided by hydrothermal minerals, mostly sulfides, but with some contribution from the transition metal oxyhydroxides. These minerals were considered to act as catalysts, that is, proto-enzymes that were subjected to the ambient redox and pH disequilibria imposed across spontaneously precipitated mineral barriers at the ancient submarine alkaline vent. More recently, the effort has been toward understanding how particular minerals, nanoparticles or clusters thereof might have exceeded the action of mere catalysts by converting these disequilibria to the internal ‘free’ energies required by a guided, though non-coded early metabolism, considerations that have led to the oxyhydroxide green rust, or more properly, fougerite, coming to the fore.

The first paper in this issue [1], Michael Russell’s ‘Prospecting for life’, describes the background chemical and geological experiences and some of the embarrassing incidents that led to, and underpin, the formulation of the ever-evolving SAVT.

The second—Simon Duval and co-workers’ [2] ‘Fougerite: the not so simple progenitor of the first cells’, addresses the present status of green rust (fougerite) as the organizing seed to all life, developing the SAVT by showing how the overall system could potentially evolve towards increasing congruency with extant life. Their model appears to satisfy the demand that each evolutionary ‘improvement’ of this dynamic system, i.e. the rarely successful ‘small jumps’ (anti-entropic thermal fluctuation traps) from one non-equilibrium steady state to the next, require that the dissipation of the driving disequilibria be increased. For as we have learnt from [3], complexification can only take place in small steps. Under this view, it follows that the progenitor of life itself has to have been complex and their argument is that fougerite is not only a mineral that was ubiquitous on our early water-world, but had the physico-chemical wherewithal to meet the requirements of a complex precursor. Indeed, the first small step was from white rust (the
simple hydroxide) to green rust (the oxyhydroxide). One vital example to be tested is that sulfate-bearing green rust could act as a pyrophosphatase. These authors imagine that negatively charged monophosphate ions pulled into interlayer nano-galleries by the positively charged oxyhydroxide layers would necessarily re-equilibrate towards substantially increased proportions of the condensed form, pyrophosphate, due to the low activity of water in these galleries. Delivering this heightened (and metastable) pyrophosphate/monophosphate disequilibrium back to the bulk phases would provide a source of free energy to protocells just as occurs in many extant cells.

Elbert Branscomb & Michael Russell [4] follow with ‘On the beneficent thickness of water’, another paper demonstrating the essentiality of having an already ‘complex progenitor’ to the first metabolizing system. In particular, this paper brings forward two generally unrecognized facts about water and life. The first is that if water were not a significantly viscous medium then neither the processes of life, nor those of its emergence in the first place, would be feasible. The second is that for this essential enabling gift of water to be manifest, the free-energy conversions necessary to support ‘matter in the living state’ must be carried out through the mediation of macromolecular ‘engines’ operating in water [5]. The essential point is that the inexplicable flux-force linearity of free-energy conversions that are mediated by macromolecules in water confers huge gains in operational efficiencies without which life would not be feasible. And the operations of a useful enzyme or prebiotic nano-engine must be fully dynamic, tightly orchestrated, highly particular and involve relative motions between parts of the engine. Notably, the operation of this kind of single-macromolecule disequilibrium converter in water is beautifully exemplified by proton-pumping pyrophosphatase, a likely key enzyme at life’s emergence as discussed in the Duval et al. contribution [2]. Branscomb and Russell also compare the structure of pyrophosphatase with green rust and similarly conclude that green rust (fougerite) makes an excellent candidate as the prebiotic nano-engine capable of the free-energy conversion of the ambient proton gradient.

Next, Martina Preiner et al. in their contribution [6] ‘Catalysts, autocatalysis and the origin of metabolism’, look to the requirement for the simultaneous activation of CO₂, H₂ and N₂ on mineral surfaces in the abiotic syntheses of such vital molecules as the amino acids, nucleic acid bases and cofactors. They show that awaruite, magnetite as well as native iron act as ‘true’ catalysts in that they facilitate the difficult reactions of the dissolved gas H₂ with the fully oxidized gas CO₂ and moderately oxidized N₂ to form pyruvate, acetate, methanol and ammonia without themselves suffering oxidation. In other words, the electrons must be derived directly from H₂—the minerals acting as prebiotic hydrogenases. They point out that these abiotic syntheses are closely aligned with the acetyl-CoA pathway and the incomplete reverse citric acid cycle employed by the anaerobic autotrophs to this day. Another exciting aspect of this work is their presentation of a plausible geochemical path from hydrogen and carbon dioxide even to nucleic acid bases. Indeed, in this emerging autocatalytic network a ghost of this prebiotic pathway may be still be discerned by the fact that CO₂ is involved still in the biosynthesis of the nucleic acid bases.

Continuing the catalytic theme, Adrian Ponce investigates the underexplored area [7]: ‘Radionuclide induced defect sites in catalysts may have accelerated the emergence of life’. Here it is pointed out that defect sites in crystal structures involved in heterogeneous catalysis often produce the most active sites for catalysis. Moreover, mineral catalysts that have been exposed to ionizing radiation from ²³⁸U, ²³²Th and ⁴⁰K are known to exhibit increased reactivity due to resultant defect sites. Such mineral defect sites exhibit high catalytic activity for the chemical evolution of organic molecules, and the hypothesis is that these processes accelerated the emergence of life and thereby should be taken into account in experimental investigations.

Yang Ding et al. follow with a demonstration of the energizing effects of [8] ‘Intrinsic concentration cycles and high ion fluxes in self-assembled precipitate membranes’ such as those encountered at submarine alkaline hydrothermal vents. Wherever life began, cycles in chemical concentration to bring basic molecular components together are seen to be important to push vital chemical reactions forwards. The authors show that compartments in alkaline hydrothermal
vents made by self-assembled precipitate membranes—they call these chemical nanoreactors warm little pores—naturally have cycles of concentration and that the flow of ions, and so of 'free' energy, across the membranes may be just right for them to be the hatchery of life.

Another experimental report by Rafaela Vasiliadou and co-workers—one using a microfluidic chip—addresses [9] ‘Possible mechanisms of CO₂ reduction by H₂ via prebiotic vectorial electrochemistry’. Sharp H⁺ gradients across Fe(Ni)S mineral membranes prefiguring both the magnitude and polarity of transmembrane electrochemical ion gradients in cells are investigated here. They show that permeability of disordered Fe(Ni)S barriers to H⁺ is six orders of magnitude greater than to OH⁻, so steep pH gradients of the order of 3 pH units are found across 20–30 nm close to the alkaline face of the barrier. In theory, these could facilitate the reduction of CO₂ by H₂ across single mackinawite nano-crystals close to the alkaline face of the barrier. Thus, at partial pressures of H₂ equivalent to those found in deep-sea hydrothermal systems the reaction should proceed exergonically especially when facilitated by vectorial cationic gradients. The advantage of these vectorial gradients as a driving force for CO₂ reduction at the origin of life is that they modulate the redox potential of H₂O–CO₂ and Fe(Ni)S with driving in a fashion that is topologically analogous and arguably homologous with cells. While this mechanism is fundamental to one approach to the alkaline vent theory, this paper makes the useful admission that while sharp H⁺ gradients should facilitate the reduction of CO₂ by H₂ across single mackinawite (FeS) nano-crystals close to the alkaline face of the barrier, the reaction did not reliably progress. The authors explain this by pointing out that the low partial pressure of H₂ at atmospheric pressure means this reduction is ‘borderline endergonic, and therefore unlikely to proceed’. The conclusion must not be taken as an experimental failure. As Vroomhofden puts it in Douglas Adams’ The hitchhiker’s guide to the galaxy [10], ‘we demand rigidly defined areas of doubt and uncertainty!’, a phrase echoing Feynman’s stringent maxim: ‘we are trying to prove ourselves wrong as quickly as possible, because only in that way can we find progress’ [11]. Indeed, Vasiliadou et al. do plead for further experimentation using a high-pressure version of their microfluidic device—a challenge surely to be accepted by a well-funded laboratory?

Following on, the contribution of Stuart Bartlett & Patrick Beckett [12], ‘Probing complexity: stochastic thermodynamics and computational mechanics approaches to origins studies’ addresses complexity in the context of the need to develop an intrinsic information and guidance system, with an eye on how such a system would be forced to evolve during life’s emergence [13]. The problem is how ‘associative learning’ could emerge in a pre-biological setting—how could rudimentary metabolism be augmented through additional reactions leading to molecular products, which would permit sensitivity to the environment? A conclusion could be that as networks to encode and process information about the ambient environment involve learning behaviour and the architecture for performing the learning and computation, these abilities must have emerged spontaneously and concurrently. Furthermore, the authors argue that current research that reveals the intimate relationship between stochastic thermodynamics and information processes provides physical bounds for how and why information and complexity would emerge and persist in prebiotic systems. This sets a challenge to experimenters and modellers to work out if, or how, fougereite could have been exploited in this way.

James Milner-White then demonstrates the logical need for [14] ‘Protein 3D structures at the origin of life’ in contrast to the assumptions required for an RNA world. Once peptides are generated, then it is possible to envision how those inorganic molecules, e.g. phosphate and the transition metals that bring inorganic chemistry to life, may have been sequestered and then contributed to the ‘free’ energy converting engines central to life’s operations. For example, Milner-White points to how the planar tripeptide, the ATCUN (amino terminal Cu¹, and Ni³)-binding motif, can also sequester Co, rendering the planar metallopeptide capable of acting as an electrocatalyst for hydrogen evolution from water—another proto-hydrogenase? [15]. Other short peptide structures, called ‘nests’, are shown to readily sequester phosphate (the metaphorical ‘egg’) through hydrogen bonds in a structure homologous with the phosphate-or P-loop, a motif found throughout all branches of life, including pyrophosphatase and ATPase. Even [4Fe-4S]⁺/²⁺/³⁺ clusters could be loosely bound in such a manner.

Robert Szilagyi and co-workers, in their contribution [16] ‘Natural selection based on coordination chemistry: computational assessment of [4Fe-4S]-maquettes with non-coded amino acids’ take an ‘evolutionary step’ forward in emphasizing the necessity of the thiolate side chain to effectively anchor an iron–sulfur cluster (the ‘egg’) in a minimum of 7- or 8-mer peptide ‘nests’. As we might expect from extant life, molecular dynamics simulations and density functional calculations revealed the superiority of cysteine in providing the strongest ligand during the spontaneous assembly of egg and nest. However, both the shorter side chain thioglycine and the longer homocysteine also had activity and could have operated at life’s emergence. But as these authors point out, there would have been strong evolutionary pressure to favour cysteine.

The penultimate paper [17] ‘On the origin of degeneracy in the genetic code by Diego Gonzalez, Simone Giannerini and Rodolfo Rosa introduces a new paradigm for interpreting genetic information’ [18]. It offers an enticing prospect to the SAVT from over the ‘event horizon’ toward a progenitor code, the emergence of the genetic code itself and to LUCA. The authors emphasize how the fundamental status of symmetry principles from the physical sciences may be brought to bear in molecular biology and evolution. That symmetry properties matter is true also of mineralogy, especially to the model of fougereite and its anionic intercalates as a precursor of life. Generally, minerals have such a high degree of symmetry that they carry little information. But fougereite has significantly lower symmetry and thus can impart some information both within its constraining structure and to any organic emanations therefrom. Indeed, speculations have been made as to the possibility that codon to amino acid side chain affinities first emerged on, or even within, crystal lattices. We can recall that Bartlett and Beckett [12] considered nano-phase minerals such as green rust as stochastic sensors with some capacity to learn about their environment. As we might expect from extant life, molecular biology and evolution. That symmetry properties matter is true also of mineralogy, especially to the model of fougereite and its anionic intercalates as a precursor of life. Generally, minerals have such a high degree of symmetry that they carry little information. But fougereite has significantly lower symmetry and thus can impart some information both within its constraining structure and to any organic emanations therefrom. Indeed, speculations have been made as to the possibility that codon to amino acid side chain affinities first emerged on, or even within, crystal lattices. We can recall that Bartlett and Beckett [12] considered nano-phase minerals such as green rust as stochastic sensors with some capacity to learn about their environment. As we might expect from extant life, molecular biology and evolution. That symmetry properties matter is true also of mineralogy, especially to the model of fougereite and its anionic intercalates as a precursor of life. Generally, minerals have such a high degree of symmetry that they carry little information. But fougereite has significantly lower symmetry and thus can impart some information both within its constraining structure and to any organic emanations therefrom. Indeed, speculations have been made as to the possibility that codon to amino acid side chain affinities first emerged on, or even within, crystal lattices. We can recall that Bartlett and Beckett [12] considered nano-phase minerals such as green rust as stochastic sensors with some capacity to learn about their environment.
In their contribution [19] ‘Isoprenoids enhance the stability of fatty acid membranes at the emergence of life potentially leading to an early lipid divide’ Sean Jordan and co-workers bring us to LUCA, or perhaps beyond. Focusing on the striking physical differences between the two inter-soluble membrane-constituting single chain amphiphiles (SCAs) comprising the contrasting membranes of bacteria (the fatty acids) and archaea (unsaturated isoprenoids with a terminal hydroxy group), they consider the possibility that these differences were responsible for the differentiation of the two domains at, or near, the emergence of life. These outstanding physical differences revealed by their experiments are thought to arise as a result of their relative stabilities in early hydrothermal environments. While the authors demonstrate that both are miscible and that both can form vesicular bilayers, the isoprenoids would continue to exist as independent vesicles whereas the fatty acids would tend to clump together and aggregate on surfaces of an alkaline hydrothermal mound. However, the concentration of isoprenoids required to make vesicles is 30-fold more than those produced by fatty acids. Nevertheless, it is attractive to assume that an indiscriminate mix of the two SCAs at the alkaline hydrothermal vent dominated by the stability-enhancing isoprenoids, was the initial state of LUCA’s membrane. In this venue, it could be imagined that the thermal and redox contrast between the interior and exterior of the hydrothermal mound would lead to a differentiation, with the proto-archaea dominating the higher temperature and more reduced interior, while the proto-bacteria would be more at home around the cooler, more oxidized, exterior of the mound. The G1P and G3P headgroups of archaea and bacteria were likely added later, an addition cementing the differentiation of the first bacteria from the first archaea proper.

In spite of the contradictions characteristic of cutting edge science, common to most of the papers is the acceptance of the original SAVT model for the emergence of life [20–22]—namely its grounding in moderate temperature hydrothermal serpentinization, an ambient proton motive force, the centrality of redox disequilibria associated with exhalative mineralization, a membrane to hold the disequilibria—taking fully into account of extant life’s requirement for a million electrons per second per cell [23].

One newer aspect considered by some contributions is that fougereite provided the organizational seed to all life [24] and thus reveals the roots of the evolutionary tree that have lain hidden for the last 160 years. The SAVT now leads research on the emergence of life as a dynamic entity, i.e. an interactive ensemble of nano-scale disequilibria-converting engines, as evidenced by references to it made in many recent books and by the rapid growth in citations. It is built on empirical evidence—e.g. the rapid reduction of nitrate (the relatively stable first likely high-potential electron acceptor) to ammonia and the amination of pyruvate to the amino acid alanine. The SAVT predicts that approximately 30 or so hydrous interlayers of green rust, clamped between layered pliable redox-active iron oxyhydroxide boundaries doped with Ni, Co and Mo and supported by iron sulfides, provide the potential to:

(i) reduce CO2 to formate,
(ii) differentiate and specialize functions such as proton-pumping and thereby generate, through a conversion engine, a far out-of-equilibrium PPi:Pi ratio of 1010!—early life’s main power source
(iii) enable electron bifurcation, bequeathing life a molybdenum-mediated step-up transformer to drive strongly endergonic reactions and thus provide the organic framework molecules required for metabolism,
(iv) oxidize hydrogen and methane with nitric oxide to methyl groups to react with formate and thereby, (v) produce the carboxylic acids acetate and pyruvate, the target molecules of all metabolism,
(vi) aminate pyruvate to alanine,

Figure 2. Sketch plotting progressive complexification against increase in the rate of entropy production to illustrate the incrementality of each of the steps as life is driven into being. Paradoxically, the increases in entropy are only made possible as ever-lower entropy structures are evolved [3,30,31]. GR, green rust; FA, fatty acid; IP, isoprenoid. (Online version in colour.)
(vii) polymerize this and other amino acids to heterochiral peptides that
(viii) protect the evolving system at its various scales, and
(ix) synthesize nucleotide polymers from simple precursors that may have acted as templates in the direct instruction of peptide growth and sequencing within fougerite galleries, so initiating the RNA world [25]; all-in-all resulting in the germination and first flowering of the organic evolutionary tree as it emerged from the hydroponically fertilized green rust seed [24].

The above geochemical and biochemical steps must interface with geophysical and biophysical steps that involve the self-assembly of semipermeable mineral membranes across which osmosis, and eventually chemiosmosis, can operate. This is a natural chemical garden, a developing field termed chemobronics [26].

So the contributions in this volume comprise a report on the standing of the SAVT for the emergence of life at 30; what has been learnt and what has been discovered. They represent a school of thought as it presently stands. Hence the papers do not review the status of hypotheses such as the RNA World, Darwin’s warm little pond, panspermia or the Urey–Miller Model, although it might be argued that the SAVT offers a severe challenge to each of these. Nevertheless, it will certainly occur to the reader that the theory still comprises a number of contradictory threads. While this may discount some, to others there will be the satisfaction of finding, through experiment or garnering from burgeoning research areas such as nano-engineering, microelectronics, fuel cell research, catalysis, material science, radiation chemistry, biophysics, stochastic thermodynamics, information theory, computational modelling and microbiology, which of these threads fail, which survive (at least for a time), and which new threads might have to be introduced or offer themselves for the model to bear increasing weight as it evolves, and our conscience examines them for consistency and correctness [27]. To quote Steven Shapin [28]:

Science is a vast fiduciary system. Scientists know what they do by finding trustworthy sources and then trusting them. It is also what Polanyi called a polycentric system, in which autonomous and only loosely coordinated groups of specialists—mildly skeptical and mainly trusting—periodically keep an eye out for what is going on next door. The coherence and integrity of the body of scientific knowledge arise through these processes of mutual adjustment. Finally, the bases of scientific judgment cannot be completely articulated because the ‘tacit’ dimension is ineliminable. It is not a fly in the formal ointment; it is what makes science science. You would understand that, Polanyi suggested, if you knew what it was like to be ‘confronted with the anxious dilemma of a live scientific issue’. The further away you are from the quotidian life of scientific practice, the more you tend to be infatuated with myths of method (see [29]).

Figure 2 gives a speculative outline of the incremental steps assumed taken toward life’s emergence based on the ideas of Endres [3] and Branscomb & Russell [30,31] as context to the contributions summarized above.

Our place in the universe begs the questions, why and how life first emerged, which have been a concern of human-kind since the first written records, and probably before that. At the practical level, as the search for extraterrestrial life intensifies, especially among the so-called water worlds, the alkaline vent theory is unique in indicating the initial conditions and disequilibria required to drive life into being and thereby the best methods of identifying the more promising candidate worlds. The SAVT, as it has been further fleshed out at the Granada meeting, provides the missing first chapter in the life and earth sciences.

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