

The “Origin-of-Life Reactor” and Reduction of CO₂ by H₂ in Inorganic Precipitates

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Abstract It has been suggested that inorganic membranes were forerunners of organic membranes at the origin of life. Such membranes, interposed between alkaline fluid in submarine vents and the more acidic Hadean ocean, were thought to house inorganic molecular machines. H⁺ flowed down the pH gradient (ΔpH) from ocean to vent through the molecular machines to drive metabolic reactions for early life. A set of experiments was performed by Herschy et al. (J Mol Evol 79:213–227, 2014) who followed earlier work to construct inorganic precipitate membranes which, they argued, would be transected by a ΔpH . They supposed that inorganic molecular machines might assemble by chance in the precipitate membranes, and be capable of using the ΔpH to drive unfavourable reduction of CO₂ by H₂ to formate and formaldehyde. Indeed, these workers detected both of these compounds in their origin-of-life reaction vessel and contend this was proof of principle for their hypothesis. However, it is shown here by a straightforward calculation that the formate produced was only that which reached on approach to equilibrium without any driving force from ΔpH . We conclude that the reaction was facilitated by isotropic catalysts in the precipitate membrane but not by an anisotropic ΔpH -driven molecular machine.

Keywords Inorganic membranes · Natural pH gradient · Hydrothermal vents · Chemiosmotic theory · Origin of life

Introduction

In all groups of modern organisms, chemiosmotic coupling (Mitchell 1966, 1968; Nicholls and Ferguson 2013) is thought to provide an important mechanism for energy conservation. For example, proton pumps using energy made available from oxidation/reduction reactions can drive H⁺ across a thin lipid membrane to generate a proton motive force (Δp) comprising both a pH gradient (ΔpH) and an electric membrane potential ($\Delta\varphi$):

$$\Delta p = \Delta\varphi - (2.303 RT/F) \times \Delta\text{pH}.$$

The negative sign arises because $\text{pH} = -\log [\text{H}^+]$. Δp can drive H⁺ back across the membrane through protein molecular machines such as the ATP synthase to generate ATP for use in metabolism. Russell and Hall (1997) suggested that at the origin of life a “natural pH gradient” might have existed across inorganic membranes somehow interposed between alkaline fluid exhaled from submarine hydrothermal springs or vents (a consequence of serpentinisation in the underlying rocks), and the relatively acidic Hadean ocean. This natural ΔpH could then have driven H⁺ from ocean to vent through primitive, inorganic molecular machines embedded in the membrane to power, for example, redox reactions or pyrophosphate synthesis needed for early metabolism (e.g. Fig. 1). Russell and Hall (1997) and Lane et al. (2010) argued that this process was crucial to the origin of life, and it later evolved into the protein/lipid systems used by modern organisms. The natural ΔpH might have been in the range of 4 U and thus capable of generating about 24 kJ of Gibbs energy mol⁻¹ of protons transferred across the membrane ($\Delta G = -F \Delta\text{pH}$), sufficient to drive coupled biochemical reactions.

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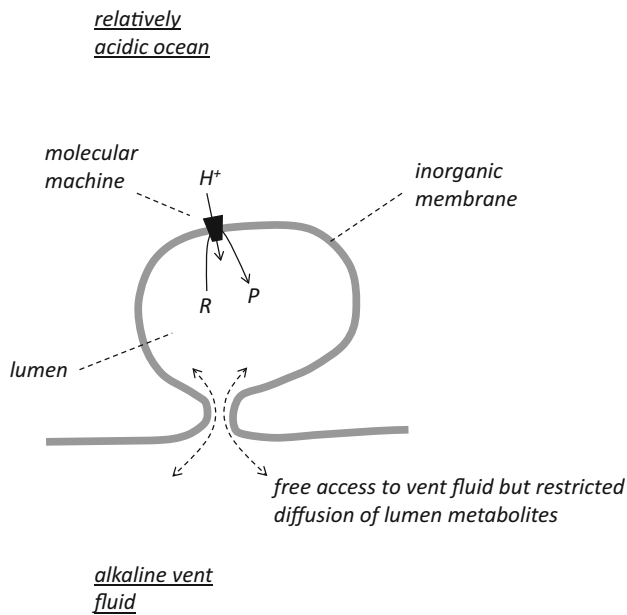


Fig. 1 Theoretical construction of an inorganic membrane at the origin of life. R = reactants of the Δ pH-consuming inorganic molecular machine, P = products. Taken from Lane et al. 2010, Nitschke and Russell 2010 and Sojo et al. 2016

Experiments to Identify Candidate Inorganic Membranes in Processes Taking Place at the Origin of Life

Inorganic membrane structures are favoured by proponents of the natural pH gradient hypothesis because of difficulties in imagining how appropriate organic molecules could be selected and continuously delivered to the emergence site of autotrophic metabolism (e.g. Mielke et al. 2011). Candidate inorganic membranes have been explored in several publications. Perhaps the most propitious are those in which a high pH solution of Na_2S and NaCl (in the presence or absence of silicate), said to be analogous to vent fluid, was passed upwards through either an aperture or needle into a solution of FeCl_2 and NaCl , said to be analogous to the ancient Hadean ocean (Russell et al. 1989; Mielke et al. 2011). A continuous colloidal gel membrane precipitated at the interface between the two solutions, and expanded into “bubbles”, “globules” and “chimney-like vertical tubes”. Freeze-dried sections of the precipitates (Russell and Hall 1997) revealed a honeycomb-like structure of smaller compartments, 10–20 μm across, that were separated by membranes, 2–3 μm thick. Wächtershäuser (2006) argued that the compartments were an artefact of the freeze-drying procedure, but this was disputed by Russell (2007). Environmental scanning electron microscopy (ESEM) of the harvested chimneys indicated a tubular structure of around 1 mm diameter and wall thickness ranging from 4 to 100 μm , typically about 20 μm

(Mielke et al. 2011). The chimney wall appeared to be formed of two layers and was therefore described as a “bilayer” though this is not to be confused with the lipid bilayer of biological membranes which has a thickness of only about 5 nm. The outer crystalline layers in the chimneys were said to define a myriad of micropores implying openings in their walls through which materials might pass but there is no evidence for this. In experiments performed in the absence of silicate, ESEM revealed other regular structures on the membrane surface, variously described as “crenulations”, “flanges” and “microdendrites”. The small (10–20 μm), honeycomb-like compartments with 2–3 μm membranes seen in the freeze-dried samples reported by Russell and Hall (1997) were not evident in the ESEM experiments of Mielke et al. (2011), and this might support the critical comments of Wächtershäuser (2006)—see above.

Few experiments have been performed to investigate the fragility, stability and ion permeability of model inorganic membranes, properties which we can expect to be of great importance to the natural pH gradient hypothesis. Filtner et al. (2003) carried out a simple experiment to test the ability of an iron sulphide membrane to maintain gradients of pH and sulphide concentration. Their membrane was formed by layering a solution of (relatively acidic) ammonium iron(II) and NaCl on to a set, relatively alkaline, agar gel containing Na_2S , NaCl and NaOH . Iron sulphide was precipitated at the solution/gel interface. Judging by the solution volumes employed in the experiment, this membrane may have been quite thick, perhaps in the order of mm. A pH microelectrode and a Pt redox probe were lowered from the upper solution, through the membrane, and then into the gel. The measured potential differences arising from the pH and sulphide gradients across the iron sulphide membrane were stable for >4 h. In a control experiment in which the ammonium iron(II) was omitted, the gradients were almost completely dissipated in <4 h. It was fair to conclude that the iron sulphide membrane acts as a barrier to the diffusional equilibration of the two solutions of different pH and E_h (Filtner et al. 2003; Mielke et al. 2011) but it might be reaching too far to state that this work provides experimental support for the view that large electric potential differences were generated across membranes between the alkaline vent fluid and the ocean on the early earth as argued by Russell (2007, 2010) and Russell et al. (2013).

Another method to examine mineral membranes that were thought to play a role in the origin of life was pursued by Barge et al. (2012). In “chemical-garden” experiments (Coatman et al. 1980), they added “seed” crystals of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ to (aerobic) solutions of sodium silicate and/or K_2HPO_4 but Na_2S was not included. A precipitate membrane immediately formed around the crystal surface and

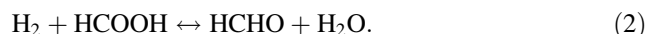
expanded as water was drawn in presumably by osmosis. Morphologies were not entirely predictable but included “hairs”, “bulbs” and “tubes”. ESEM images indicated that the bulb membrane was 10–20 μm thick.

How one or more of these phenomena might have led to the deposition of membranes that isolated vent fluid from the ocean at the origin of life is an open question. Four models of the ancient membranes are concurrent: (i) the “inorganic pore” (Lane et al. 2010; Nitschke and Russell 2010; Sojo et al. 2016), (ii) the “sea-floor mound” (Russell and Hall 1997; Russell 2007; Nitschke et al. 2013), (iii) the “lodged vesicle” (Sojo et al. 2014) and (iv) the “labyrinthine network of microcompartments/micropores” (Lane and Martin 2012; Sousa et al. 2013; Herschy et al. 2014; Sojo et al. 2016). In some articles from the groups of MJ Russell, W Martin and N Lane (the “RML” groups), a generic “inorganic membrane” or “inorganic barrier” is used for descriptive purposes; I will adopt that practice here.

ΔpH -Utilising Molecular Machines

In the hypothesis, it is proposed that that inorganic molecular machines embedded in the inorganic membrane can use the energy of the natural ΔpH to drive useful chemistry. The ΔpH -consuming molecular machines are also described as nanoengines (Russell et al. 2014; Barge et al. 2017). Such inorganic molecular machines capable of coupling the energy of the natural ΔpH to a chemical reaction must have been complex assemblies at the molecular level. According to the hypothesis of Russell and Hall (1997), the machines would have been synthesised by chance in inorganic membranes, and in quantities sufficient to form a stable population in the vent. Herschy et al. (2014) followed a radical and direct approach to test this expectation. They used a procedure similar to that of Russell et al. (1989) and Mielke et al. (2011) to produce iron sulphide/iron hydroxide chimneys, assuming that their experimental conditions would favour the formation of pH gradients across the walls of the chimneys, and the chance formation of ΔpH -consuming inorganic molecular machines within those walls. They chose to look for molecular machines capable of reducing CO_2 to formate and formaldehyde with H_2 and using the energy of the expected ΔpH . These reactions had previously been suggested by the RML groups to have had an important role in an autotrophic beginning to life in alkali vents (Russell 2007; Martin and Russell 2007; Nitschke and Russell 2009; Russell et al. 2013; Lane 2014).

In the *absence* of a coupled energy supply such as a ΔpH , H_2 is a poor reductant in the following reactions:



At pH 7.0, both equilibria lie to the left-hand side of the equations: the standard redox potential (E'_0) for the $2\text{H}^+/\text{H}_2$ couple is -414 mV, for $\text{CO}_2/\text{formate}$ it is -430 mV and for formate/formaldehyde it is -580 mV (values cited by Lane and Martin 2012).

Through drilled holes in the floor of their “origin-of-life” reactor kept under an atmosphere of N_2 , Herschy et al. (2014) infused a solution of $\text{Na}_2\text{Si}_3\text{O}_7$, K_2HPO_4 and Na_2S (pH ≈ 11 , 70°C), “vent fluid”, into an “acidic ocean” of FeCl_2 and NiCl_2 (pH ≈ 5 , 20°C)—compare with Mielke et al. (2011). The N_2 was admixed with 2% H_2 and the ocean fluid was supplemented with NaHCO_3 as substrates for their expected reactions described by Eqs. (1) and (2). The infusion led to the formation of thread-like precipitates from the drilled holes, probably similar to the chimneys of Mielke et al. (2011). The precipitates, however, were thought to be composed mainly of ferrous silicates and phosphates but some harvested samples contained small crystals which, on the basis of their crystal-plane spacing, might have been the mineral, mackinawite, $\text{Fe}(\text{Ni})\text{S}$. The thread-like precipitates were thin-walled hollow-tubes, initially with outside diameters of 2–3 mm but thickening to about 5 mm after several hours. We may suppose that the wall thickness was similar to that in the chimneys of Mielke et al. (2011), perhaps around 20 μm . The flow of the alkaline fluid during infusion was proposed to have set up a ΔpH across the precipitated tube walls, and it was hypothesised that inorganic constituents in the walls could have spontaneously assembled into molecular machines capable of utilising the pH gradients to drive production of formate and formaldehyde from CO_2 . In samples collected close to the precipitates, Herschy et al. (2014) did indeed claim to find low micromolar concentrations of formate, and low nanomolar concentrations of formaldehyde.

This seems to be an exciting finding that Herschy et al. (2014) described as a “proof of concept” for the natural pH gradient hypothesis. However, the results require some careful consideration. We can precisely calculate the concentrations of formate and formaldehyde that would have been produced at equilibrium from CO_2 and H_2 in the presence of a simple catalyst but in the *absence* of any pH gradients across structures in the precipitates that might drive the reactions. In the experiments of Herschy et al. (2014), the pH of the reactor solution was not recorded during infusion but judging from the dominant buffers present in the system (phosphate and bicarbonate, see above), we will assume that it probably fell in the neutral range. For the purpose of our test calculations we shall first assume a pH of 7.0 throughout the vessel, and in aqueous

solutions within the walls of the precipitates (thus maintaining $\Delta\text{pH} = 0$). Below we shall then briefly summarise the results of similar calculations at a broader range of pH. From Henry's Law and the Nernst equation, the redox potential (E_h) of the $2\text{H}^+/\text{H}_2$ couple at pH 7, and an H_2 partial pressure of 0.02 atmospheres, is -363 mV which will have remained approximately constant in the vessel at the controlled gas pressures of the experiment (affected only by the slow change in the solution pH during infusion). The temperature of the reaction vessel was not controlled in the Herschy reaction vessel but we have assumed that it remained close to that of the starting temperature of the "ocean" solution (see above).

We shall firstly take the reaction described by Eq. (1). In our test calculation, we shall assume that some material(s) in the precipitates could have *catalysed* the reaction but *not* that the catalytic material could have operated as an inorganic molecular machine utilising the ΔpH across an inorganic barrier. The E_h of the $\text{CO}_2/\text{formate}$ couple in the vessel before infusion began would have been indeterminately high since the formate concentration was close to zero. During infusion, and as the reaction proceeded, the E_h of this couple would have fallen as the CO_2 (NaHCO_3) was reduced to formate. Since we are assuming no driving force from ΔpH in this test calculation, the E_h of the $\text{CO}_2/\text{formate}$ would eventually (at a rate depending on the effectiveness of the catalyst) have approached the -363 mV of the $2\text{H}^+/\text{H}_2$ couple (see above), as the reaction came to equilibrium. At this point, the Nernst equation can be applied to the $\text{CO}_2/\text{formate}$ couple. It is assumed that the E'_0 , cited by Lane and Martin (2012), was measured when the concentration of formate equalled the total concentration of carbonates (see Reda et al. (2008) for a more comprehensive discussion), and we have used the equation according to this understanding. In this way we calculate that, for the NaHCO_3 starting concentration of 10 mM used in the experiment, the formate would have attained a concentration of about 58 μM at equilibrium. This shows that the estimated low micromolar formate determined by Herschy et al. (2014) in their vessel could easily have been reached on the approach to equilibrium even with *no driving force from a putative ΔpH* . Thus, there is no support from these data for the suggestion that CO_2 reduction to formate by H_2 in the vessel was driven by a ΔpH across an inorganic barrier/membrane such as the walls of the thread-like precipitates. The result of this elementary calculation does not demand either the juxtaposition of alkaline and acidic solutions across inorganic barriers or the spontaneous assembly of a ΔpH -powered inorganic molecular machine.

We have also repeated the calculation at pH 6.0 and 8.0 making the same assumptions. The redox potential of the H^+/H_2 couple at each of these pH values was simply

determined from the Nernst equation. Because of pK_a effects, the dependence of the midpoint potential (E_m) of the $\text{CO}_2/\text{formate}$ couple on pH is more complicated. Thus, the slope of the E_m versus pH profile changes in the pH range 6–8 as the reaction shifts from $2\text{e}^-/\text{H}^+$ to $2\text{e}^-/2\text{H}^+$. We have therefore applied the data from Reda et al. (2008) to the values cited by Lane and Martin (2012), calculated the E_m values at pH 6.0 (-395 mV) and pH 8.0 (-500 mV) and hence the concentrations of formate reached if the reaction of Eq. (1) had reached equilibrium. The results of the calculations are that 8.5 μM formate would have been produced at equilibrium in the reactor at pH 6.0, and 27 μM at pH 8.0. The calculated values at pH 6.0, 7.0 and 8.0 fall well within the precision indicated by the Herschy et al. report of "low micromolar concentrations". Again, we see no evidence for a driving force from a ΔpH .

To provide an indication as to how far a ΔpH -utilising molecular machine *could* drive the reaction, we shall now consider the situation from a different perspective. We shall assume that the precipitates of Herschy et al. (2014) were transected by a ΔpH and that they *did* house molecular machines capable of using that ΔpH to drive the reaction described by Eq. (1). We shall adopt the machine stoichiometry shown in Fig. 1c of Herschy et al. (2014) with 2 scalar H^+ released on the vent side, and 2 scalar H^+ taken up on the ocean side, per 2 electrons transferred from H_2 to CO_2 . In an illustrative example, we shall select a modest ΔpH of 2 U. An extension of the calculation described above, and assuming a reaction pH of 7.0, reveals that the machine would have then been capable of driving the formate concentration up to 8.5 mM—more than two orders of magnitude greater than the calculated equilibrium concentration (for $\Delta\text{pH} = 0$, see above), and the *measured* concentration in Herschy et al. (2014): the reaction would have been driven almost "to completion". This large effect from such a modest ΔpH makes it very unlikely that an increase in the formate concentration beyond the equilibrium position might have been lost in the experimental error in the Herschy experiments.

Unfortunately, the experiments of Herschy et al. (2014) do not provide a proof of principle for the natural pH gradient hypothesis.

Now we briefly turn to the suggestion that formaldehyde was produced from formate and H_2 driven by a ΔpH in the experiments of Herschy et al. (2014). Similar calculations to those outlined above and on the reactions described by both Eqs. (1) and (2) show that only about 3 pM formaldehyde can be generated on the approach to equilibrium in the absence of any "external" energy source such as a pH gradient serving as a driving force. This is much less than the "low nanomolar" concentrations

reported by Herschy et al. which might therefore be taken as evidence *for* a ΔpH -driven reaction by a molecular machine. However, in light of their observation that the “formation of formaldehyde is variable and inconsistent between runs”, we should be cautious. In a recent essay, Wächtershäuser (2016) points out that the trivial explanation of formaldehyde appearing as a contaminant in their experiments was not considered by Herschy et al. (2014). He recalls that an earlier report that CO_2 reduction by ferrous ions and UV light gave rise to nanomolar concentrations of formaldehyde (Borowska and Mauzerall 1988) was later retracted: the formaldehyde was found to have arisen as the result of “omnipresent” contamination (Borowska and Mauzerall 1991; Mauzerall et al. 1993). Wächtershäuser (2016) emphasises that control experiments with $^{14}\text{CO}_2$ should have been performed by Herschy et al. (2014) to follow the transfer of carbon into the formaldehyde. I concur with this view. McCollom (2016) has used a similar procedure (but with a ^{13}C label and using gas chromatography–mass spectrometry) to follow the reduction of CO_2 to CH_4 , during the serpentinisation of olivine, thus unambiguously determining the origin of the reaction products. Until such experiments are performed, the proposed chance assembly of an inorganic molecular machine in the chimney precipitates capable of utilising ΔpH to drive H_2 -dependent reduction of CO_2 to formate and formaldehyde (Herschy et al. 2014; Lane 2017) can only be speculation.

Discussion and Conclusions

In his rebuttal of criticisms of the natural pH gradient hypothesis made by Jackson (2016), Lane (2017) places great emphasis on the findings of Herschy et al. (2014). He states in summary that “a pH gradient across a simple crystalline array ... should drive the reduction of CO_2 ... and this is what we have reported [in Herschy et al. (2014)]”. However, our simple calculations that are described in the present article clearly show that reduction of CO_2 to formate in the inorganic precipitates of Herschy et al. (2014) proceeds only to equilibrium, and that there is no evidence of any driving force from a ΔpH . Moreover, Wächtershäuser (2016) points out that, without appropriate supporting experiments using ^{14}C tracer, there is every likelihood that the low nanomolar concentrations of formaldehyde detected in the experiments of Herschy et al. (2014) arose as a contaminant.

We may note that iron and nickel sulphides are known to catalyse electrochemical (as distinct from chemiosmotic, Δp -driven) reduction of CO_2 to formate, CO, methanol, acetate, pyruvate and methane (Vladimirov et al. 2004;

Yamaguchi et al. 2014; Roldan et al. 2015). Such mineral catalysts might have had a role in the production of formate up to chemical equilibrium in the Herschy precipitates quite without the intervention of a ΔpH .

We must carefully distinguish between simple, inorganic catalysts and purported, ΔpH -utilising, inorganic molecular machines at the origin of life. Simple catalysis can be isotropic, molecular machines would be anisotropic, with more demanding structural requirements. Their component reactions would have involved organisation within and across a hypothetical inorganic membrane, with gating steps to effect specific coupling between the scalar and vectorial chemistries (see Mitchell 1966, 1968).

Herschy et al. (2014), Sojo et al. (2016) and Lane (2017) describe an interesting device which they argue would catalyse the ΔpH -driven reduction of CO_2 by H_2 . The hypothetical device has inorganic catalytic centres for H_2 oxidation specifically located on the alkali side of the inorganic membrane, and which release protons, and for CO_2 reduction on the acid side, which take up protons. There is a pathway for two-electron transfer linking the two centres across the membrane. The dimensions of the electron transfer pathway “do not matter” (Lane 2017) but might have been up to 20 μm (the probable thickness of the membrane, see above), and could therefore comprise a chain or array of perhaps several thousand metal sulphide clusters. In this author’s opinion, the assembly, and in the light of our calculations (above), the operation of such a complex device in the inorganic precipitates of Herschy et al. (2014) are very unlikely. Our description of the Herschy device as a ΔpH -utilising molecular machine does not (*pace* Lane, 2017) misrepresent that device but simply applies a working definition. Lane (2017) claims there are other misrepresentations of the natural pH gradient hypothesis in Jackson (2016) but these seem to stem from divergences amongst various publications from the RML groups which describe the same phenomena in different ways, for example, the proposed structure models of inorganic membrane systems at the origin of life (referred to above). If the views of the RML groups have evolved over the decades (Lane 2017), it would be helpful to know from a clear exposition which have been abandoned, which now hold sway, and on what basis. In disagreement with Lane (2017), I maintain that it is justifiable to analyse the principles of the natural pH gradient hypothesis at the origin of life with only minimal reference to speculations on early metabolism or to discussion of much later events associated with the arrival of the last universal common ancestor. Furthermore, despite the assertion of Lane (2017), there are no basic errors in the calculations of Jackson (2016); indeed, apart from some illustrative and justifiable one-line approximations, there are no calculations.

Nevertheless, it is agreed with Lane that a strong experimental approach will be necessary to make progress in our understanding of how life on earth began, and specifically, for example, to better evaluate the natural pH gradient hypothesis. In this sense the attempts of Herschy et al. (2014) should be acknowledged. However, the balance of available experimental evidence currently seems to favour a “heterotrophic” rather than an autotrophic origin of life. The elegant experiments of Sutherland and colleagues (Powner et al. 2009; Sutherland 2016), for example, show that activated nucleotides and amino acids can be synthesised from simple precursors under conditions that might well have existed on earth 4.2 billion years ago. A knowledge of this chemistry, which greatly adds to the classical observations and ideas initiated by Miller (1953) and Urey (1952), and follows a long, distinguished research history, begins to provide an explanation for a plausible start to the assembly of oligonucleotides and small peptides in an RNA (Gilbert 1986) or an RNA–protein world. Colleagues favouring an autotrophic origin of life have frequently remarked upon the interesting similarities between some metal and metal sulphide centres in minerals, and those in some modern proteins, and have often described them as evolutionary relics. They imply that, at the origin of life, such minerals, in the absence of proteins, might have had a role in prebiotic metabolic cycles having autocatalytic characteristics (Martin and Russell 2007). Difficulties with this view have been summarised by Orgel (2008). A more likely explanation for these inorganic evolutionary relics is that they were captured by proteins *after* the emergence of genes and gene-translation systems. Environmental selection pressures were then able to guide a Darwinian evolution, away from the Sutherland chemistry, and to channel the functions of metallo- and other proteins towards the development of the metabolic pathways that catalyse biosynthesis, including CO₂ fixation and energy transduction mechanisms, similar to those found in modern-day organisms. This view would disfavour the notion that the site of the origin of life was in submarine vents but was rather in a freshwater environment, for example, in hydrothermal fields (Deamer 2017).

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Compliance with Ethical Standards

Conflict of interest There is no potential conflict of interests.

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