

# On the emergence of life via catalytic iron-sulphide membranes

Michael J. Russell<sup>1</sup>, Roy M. Daniel<sup>2</sup> and Allan J. Hall<sup>1</sup>

<sup>1</sup>Department of Geology and Applied Geology, University of Glasgow, Glasgow G12 8QQ, UK,

<sup>2</sup>School of Science and Technology, University of Waikato, Hamilton, New Zealand

## ABSTRACT

We propose that the precipitation of a gelatinous iron-sulphide membrane is the necessary first step towards life. Membrane vesicles were inflated with alkaline, sulphide-bearing hydrothermal (<200°C) solution and grew on a submarine sulphide mound in acid iron-bearing Hadean seawater. Once a critical size had been reached (0.1–1 mm) vesicles would have budded contiguous self-similar daughters. We assume that the membrane was rendered insulating by the adsorption and/or oxidative precipitation of organic and organosulphur compounds. As a consequence of the naturally induced proton-motive (chemiosmotic) force, and the activity of the iron monosulphide redox catalysts within the membrane, organic compounds would have accumulated within the vesicle. Osmotically driven growth therefore became more significant with time. The geochemical environment envisaged as responsible for this first step towards life is consistent with that widely accepted for the early Earth.

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## PROPOSAL

The biggest gap in the theoretical proposals bearing on our understanding of the emergence of life is that between the prebiotic generation of organic chemicals and the origin of the earliest cell. Given the probable low yields of abiogenic organics in hydrothermal solutions (Shock, 1992a) what would first cellular membranes be made of? We propose here that iron-sulphide membranes were the earliest stage in the evolution towards reproducing cells and that they were generated at hot (<200°C) sulphide-bearing alkaline (pH 9) springs entering the mildly oxidized, acidic (pH 5.5) Hadean ocean (Macleod *et al.*, 1993). The iron-sulphide membranes formed vesicles which grew initially by hydrothermal inflation, but evolved a capacity for growth and 'reproduction' by osmotically driven

swelling and budding. Such a beginning of life is at one with the generally accepted conditions in and on the highly reduced early Earth where hydrospheric and atmospheric water, carbon dioxide and nitrogen were the oxidants. Kinetic barriers to complete reduction of these substances are responsible for the hydrothermal generation of a variety of metastable organic molecules, though in limited concentrations (Shock 1992b).

Although sparse, sufficient prebiotic organic molecules would have been present in the hydrothermal solution to be included in, or absorbed onto, the nascent gelatinous membrane, so that, despite its iron sulphide content, it was relatively non-conducting. Therefore, the separation of the alkaline spring water from the acid ocean by the iron-sulphide membrane could act as a major additional (chemiosmotic) energy source, driving the transport of seawater

organics into the vesicle (Mitchell, 1979; Koch and Schmidt, 1991). The importance of iron sulphides in catalytic reactions in life's origins is widely accepted (Russell *et al.*, 1988 Wächtershäuser, 1988; Drobner *et al.*, 1990; da Silva and Williams, 1991; Cairns-Smith *et al.*, 1992; and see Hall *et al.*, 1971 and Müller *et al.*, 1985).

Our proposal thus comprises, within a simple entity: a catalytic surface; an enclosure for concentrating the organics necessary for the development of metabolism; and a potential energy mechanism of the type (i.e. chemiosmotic) used by modern organisms (Mitchell, 1979).

## MEMBRANES

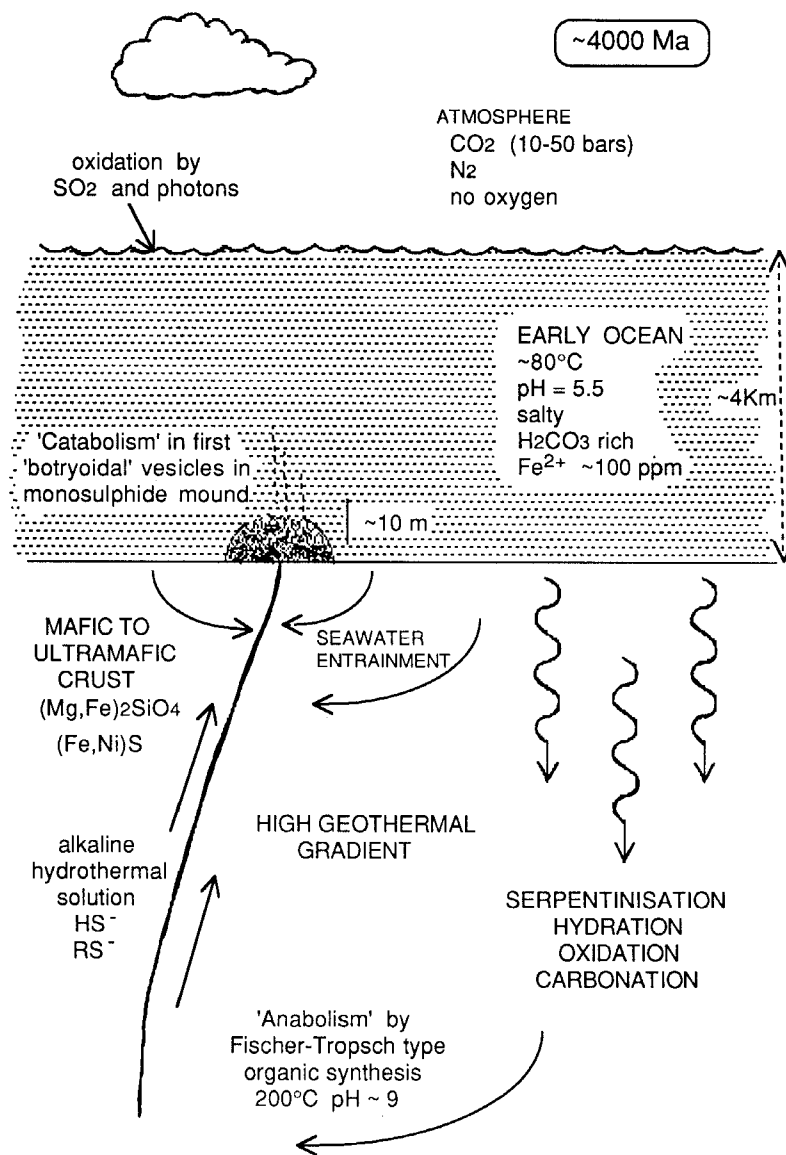
In a previous contribution we demonstrated how gelatinous membranes could be precipitated at fluid interfaces, for example by introducing sodium sulphide solution into a solution of ferrous and ferric chloride, an experiment first designed to mimic the formation of hydrothermal chimneys in sedimentary exhalative base metal deposits (Russell *et al.*, 1989). Apart from fine hollow spires of iron sulphide, contiguous 'bubbles' (vesicles) also formed, comparable to sulphide structures fossilized as hollow pyrite botryoids, about 1 mm across, found in some of these ore deposits (Fig. 1). The advantage of this process of growth is that it side-steps kinetic barriers required for nucleation or crystallization, and that it could be self-referencing. The source of supply of solute to the membrane, trapped as it is within the vesicle, is always administered directly to any leakage point, to develop a daughter vesicle. In the Hadean, an ideal site for membrane growth would be at the interface between thiolate-bearing ( $RS^-$  and  $HS^-$ ), alkaline, reduced hot spring waters and a mildly oxidized, acid, iron-bearing



**Fig. 1.** Hardened iron sulphide (pyrite) bubbles or botryoids 0.2 mm across and 350 million years old from the Tynagh mine in Ireland (Banks, 1985). Such structures, comparable with those in Fig. 4, but generated at hot springs 4 billion years ago, are envisaged as predecessors to the first cells (vesicles). Note that the iron sulphide membranes are grossly thickened by subsequent overgrowth of pyrite, except near the base of the botryoids and in the floating remnant to the left. We assume that these membranes were originally composed of colloidal iron-monosulphide.

ocean (Macleod *et al.*, 1993) (Figs 2 and 3). The system is therefore far from equilibrium and in a steady state. It is also long-lived ( $>10^6$  yr; Russell, 1983) in contrast to black smoker systems.

Initially, growth of the membranes would be by hydrothermal inflation, with cleavage of the membrane leading to daughter outgrowths by self-seeded precipitation (Fig. 4). Later, selection would have favoured those vesicles where inflation was augmented by osmosis. Given the long-term compositional stability of the two fluids concerned (acid seawater and alkaline hydrothermal solution), the composition of the membranes, both of parent and daughter alike, will be dependent upon the physical environment and the way this governs the self-insertion/adsorption of organics into or onto the membrane.

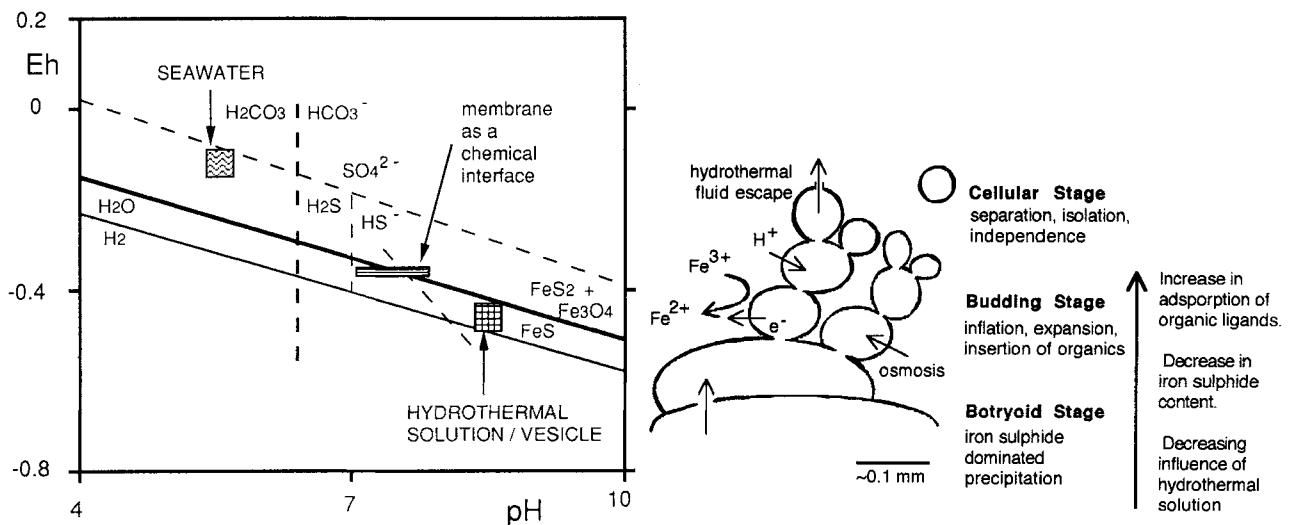


**Fig. 2.** Sketch of the natural convection system envisaged for the Hadean Sea unrelated to spreading-centre volcanism. The hydrothermal solution is seawater modified by interaction with the mafic crust and rendered alkaline by dissolution of calcium and some sodium and potassium. The early ocean itself has a relatively low pH because of the solution of atmospheric carbon dioxide released from the mantle during massive volcanic activity (Walker, 1985; Macleod *et al.*, 1993). A sulphide mound could be at least a kilometre across.

### ORGANIC SYNTHESIS

We assume that limited abiogenic production of organics, especially organosulphide compounds, were provided by Fischer-Tropsch-like reductive or polymerising syntheses (Storch *et al.*, 1951; Ferris, 1992; Shock, 1992a and b)

within the free hydrothermal convection systems operating in the magnesium-silicate-rich crust of the early Earth (Russell, 1992); that is, most of the anabolic activity was provided within the submarine hydrothermal system. A later evolutionary development in such a system would be the metabolism of



**Fig. 3.** (Left) Tentative Eh-pH diagram indicating the electro-chemical gradient between early seawater and the hydrothermal solution across the  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  sulphide membrane. The solid sloping line indicates the upper stability of FeS (co-existing with pyrite) calculated for the  $f\text{S}_2$  of the  $\text{FeS} + \text{FeS}_2 + \text{Fe}_3\text{O}_4$  buffer (PPM) at  $25^\circ\text{C}$ , 1 bar. The Eh of the membrane is represented by a horizontal band at the intersection of the PPM line and the aqueous  $\text{Fe}^{2+}$ /insoluble  $\text{Fe}^{3+}$  line (dashed). The Eh contrast would have provided about 0.2 eV potential to initiate and drive a protocell's rudimentary metabolic processes. Further energy input would be from the catabolism of hydrothermal organic compounds. The vesicle membrane exists at a low Eh and low  $f\text{S}_2$  within the stability field of mixed-valence ferrous/ferric sulphides which could have evolved to ferredoxins.

**Fig. 4.** (Right) Proposed growth of iron-sulphide membranous structures, showing development from the botryoidal stage in the hydrothermal mound towards an independent, organic-dominant cell. The independent existence of the 'cellular' stage may not have arisen until the order of 100 million years after the formation of the first botryoids.

organic products catalysed by iron sulphides, as successful colonies of vesicles gained more autonomy and independence from the immediate hydrothermal environment (Fig. 4).

However we suggest that organic synthesis could also have occurred within the body of the sulphide mound (a kind of protomicrobialite, cf. Kempe *et al.*, 1991) just beneath the membranous outermost zone of the mound using energy from the  $\text{FeS} \rightarrow \text{FeS}_2$  transition (Wächterhäuser, 1988, 1992). As time passes, crystallization to form pyrite will occur in the membrane, as this most noble of sulphides would not lend itself to reduction back to monosulphide (Cairns-Smith *et al.*, 1992). The membrane would then become dysfunctional, i.e. permeable, conducting and inflexible. It is at this later stage in the mound's development that the reactions proposed by Wächterhäuser could have occurred, resulting organics passing 'downstream' to the young vesicles on the surface of the mounds.

In addition to surface effects, a gelatinous ferrous/ferric sulphide membrane provides the potential for catalysis

by limited lateral electron transfer in vesicles, before the evolution of ferredoxins (Fig. 3). Iron sulphur proteins are invariably present in living organisms, and Hall *et al.* (1971) have suggested that these are primordial catalysts. Daniel and Danson (in prep.) have suggested they were an evolutionary predecessor to the use of NAD(P) as a redox coenzyme. Iron sulphur proteins are effective and versatile redox catalysts and Bonomi *et al.* (1985) have shown that simpler, non-protein ligands such as mercaptans and thiophenols are also effective chelating agents for iron-sulphur clusters, albeit within a more restricted redox range. Such preferredoxins can be produced in the laboratory under similar conditions to our own experiments (Bonomi *et al.*, 1985).

#### GROWTH AND REPRODUCTION

What compounds would have encouraged budding rather than continued increase in size? We know phosphate inhibits the growth of iron-sulphide membranes (Russell *et al.*, 1989). Some

phosphate or thiophosphate complexed with organics is to be expected in alkaline waters coursing through volcanic piles (Stanton *et al.*, 1978). Precipitation and sequestering of colloidal clusters of iron phosphate within the iron-sulphide membranes might have provided preferential sites for eruption of the hot alkaline fluid and consequent budding (Fig. 4). The phosphate-bounded channel could exert some control over the membrane forming at the interface of the two fluids.

Gradually, and as a result of evolution, growth by hydrothermal inflation will be augmented, and eventually superseded by osmosis. In both inflation and osmosis the surface of the membrane will act as an absorbing or precipitating surface for abiogenic organic compounds (Russell *et al.*, 1990). There are three possibilities which could be the driving force for osmosis; first, organic molecules, some of which will enter by diffusion, and be cleaved catalytically at the membrane surface inside the vesicle, maintaining the low water activity and therefore adding to the internal osmolality; secondly, hydrophobic compounds

capable of dissolving in the membrane could be converted in the membrane to a hydrophilic moiety, possibly by a redox reaction or by ionization, with a fraction of the product(s) diffusing into the vesicle interior; thirdly, organics transported into the vesicle by any chemiosmotic gradient. These products would not be removed but would be maintained at a relatively constant level by osmotic dilution as the vesicle grows, buds and produces offspring. Not all the catalytic conversions would have been destructive or catabolic; with the iron-sulphide membrane acting as a redox catalyst, oxidation and concomitant polymerization of sulphur-containing prebiotic organic molecules could also have taken place at the internal surface. Eventually vesicles could grow, divide, or fuse as described by Morowitz *et al.* (1991).

In a steady state, hydrophobic, or better still amphipathic (one end hydrophobic, the other hydrophilic) molecules can be expected to self-insert into such a hydrophobic membrane and the compounds inserted will depend on the membrane's composition. Both surfaces of the membrane will have a role as a minimal protoinformation system. The more successful the membrane interior surface is in preventing the egress of cleaved organic species then the faster will be osmotically driven growth. The more successful the exterior surface is at 'controlling' self-insertion of adsorbed organics, then the more likely any daughter cell is to resemble the parent.

The iron-sulphide membrane would age and lose its expansivity and its insulating properties by thickening and crystallization. We propose that any voids were filled by preferredoxins and abiogenic organic compounds, attracted to the membrane by surface effects or filtering, and possibly rendered less soluble by catalytic oxidation in or on the membrane [as for example in the oxidation of ethyl dithiocarbonate (aqueous solubility 8 moles per litre) to diethyl dixanthogen (aqueous solubility  $3.1 \times 10^{-5}$  moles per litre) (Poling, 1976; Dawson *et al.*, 1986) and in oxidative thioesterification (de Duve, 1991)].

#### CONCLUDING REMARKS

Our proposal does not purport to have resolved the issues of modern life's complex information and catalytic sys-

tems, but rather to have provided a credible geochemical environment within which such systems could have begun to develop. It is possible to view our proposal as fitting between those dealing with the role of crystalline mineral surfaces including pyrrhotite (Cairns-Smith, 1982; and see Wächtershäuser, 1992) as templates for the formation of organic molecules, and those dealing with vesicles constructed from biological macromolecules (see Fox and Dose, 1977). This proposal may also be regarded as a special case of the evolutionary biogenesis proposed by Morowitz *et al.* (1991).

The main features of the membrane system proposed here are its relative independence from organic molecules; self-similar reproduction during budding; contiguity; catalytic nature; and role in maintaining a chemiosmotic gradient. We conclude that life originated by continual growth of a self-referencing membrane which comprised a natural, evolving automaton - 'the membrane is the message'.

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