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Why Does Life Start, What Does It Do, Where Will It Be, And How Might We Find It?

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Abstract

A theory of how life emerges is couched in the context of the gravitational differentiation of terraqueous worlds massive enough to have held a carbon dioxide and nitrogen atmosphere. On the early Earth the differentiation to the various spheres—core, mantle, asthenosphere, lithosphere, hydrosphere and atmosphere—was largely a response to radiogenic and gravitational heat production in the interior. An effect of these density differentiations was to gather electrons in the core in native iron (Fe^0 with its full compliment). However, early core formation still left the upper mantle relatively electron-rich (in Fe^{II}-bearing minerals), compared to the exhaling and accreting oxidized volatiles (H_2O, CO_2, N_2, NO, SO_2, P_4O_{10}) that composed the early hydrosphere and atmosphere. The atoms comprising these oxidized molecules are forced to share electrons covalently, rendering some of them potential 'electron acceptors'. Hydrothermal H_2 acted as the carrier gas of electrons derived from the reduced iron in the crust. Reductions (hydrogenations), particularly of marine CO_2, NO (or NO_3^-) and Fe^{III} at alkaline submarine hydrothermal springs, led to the emergence of metabolic pathways, first in inorganic compartments, then in prokaryotic cells that multiplied exponentially to produce the early biosphere, the last sphere to differentiate (cf., Takai et al., 2004). At the larger scale of the solar system the volatiles differentiate from the sun outwards in response to the solar wind, radiation, the decline in the gravity field and condensation and sublimation. But again, the same tensions between the CO_2-bearing waters and hydrothermal H_2 would tend to drive life into being on other rocky terraqueous globes like Mars and perhaps on Europa and Enceladus (Russell and Hall, 1999; Vance et al., 2007). Without this geochemical potential there would and will be no life, for life is not the convergence of

a myriad of organic molecules but a resolution of redox and pH tensions in an aqueous environment whereby simple organic molecules are first synthesized from CO_2 and other minor entities before being polymerized, interacted with and even hydrolyzed. The unambiguous effluents from early cells would be acetate or acetic acid and its derivatives. Beyond the solar system the same logic applies. Only those extra solar planets with rocky interiors and hosting surface or ground waters containing dissolved carbon dioxide (dosed with nitric oxide) will have an accompanying biosphere, one that would be forced to emerge to resolve these same geochemical and electrochemical tensions.

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1. Introduction

"I believe a leaf of grass is no less than the journeywork of the stars"
Walt Whitman 1900

We tend to be overly bemused by the complexity of life and our place in it. It has been commonly assumed that life's emergence must be a rare, or even unique event, culminating—as we liked to think—in us. But science has continually eroded conceits about *our* place in the Universe while, at the same time, revealing more of its wonders. We ourselves are a seemingly improbable amalgam of highly complex interacting cells. However, in the greater scheme of things we pay our way in driving our planet to a more probable state, i.e., we expend energy like there is no tomorrow and produce mountains of waste, fulfilling the entropic imperative (Martyushev and Seleznev, 2006; Russell, 2007).

The best way to get to grips with the origin-of-life puzzle is to try to figure out what drove our ultimate ancestor into existence. Perhaps we can delve further back than Pooh-Bah's "protoplasmal primordial atomic globule" (Gilbert and Sullivan, 1885). Here we will develop the idea here that our ultimate ancestors were housed in inorganic compartments composed of silica, silicates, carbonates and hydroxides, with a sprinkling of metal sulfides with catalytic potential: that we were spawned from a hydrogen- and hydrogen sulfide-bearing formative fluid issuing through cracks in a serpentinizing ocean crust into the earliest carbonic ocean (Russell et al., 1989). On the interaction of the two fluids a hydrothermal mound grew over the hydrothermal vent. This mound inhibited much further

communication, excepting partial penetration by hydrogen ions, carbon dioxide, phosphate and nitrate from the ocean. It was in such a milieu that we consider the hydrogenations began that led to life's emergence.

Our exploration of this idea will lead us to conclude that life must be as common as hydrothermal convection cells on icy, wet rocky starlit planets large enough to hold an atmosphere, or at least a carbonic ocean, both in our solar system and in commensurate systems beyond. Tyler (2010) shows that liquid oceans are likely to be common on icy planets and moons, through dissipation of tidal flow energies. Nevertheless, the newly discovered water world, GJ 1214b just 13 parsecs away may be disappointing in this respect (Charbonneau et al., 2009). Its high mass (6.5 times that of the Earth), the smallness of its dwarf star and its envelop of hydrogen might restrict life there to a deep biosphere, even supposing there were a rocky interior to the planet. And any such biosphere would depend on the availability of carbon dioxide dissolved in its hydrosphere. However, were such a terraqueous globe be found to harbor life, the natures of the basic metabolic pathways would, we contend, be found to be similar to those operating here on Earth, with only the chiral handedness being indeterminate.

Both hydrothermal convection and metabolic cycles are causally connected dynamic structures that emerge as a means of dissipating energy; first physically, then chemically, before biological systems could hold sway across the surfaces of a wet planet. The notion of prebiotic molecules is demoted here to indicate merely those molecules that are produced *in situ* immediately prior to their entrainment and survival in a metabolic system. Metabolic pathways and cycles involve these simple molecules as active, somewhat ephemeral players in an evolutionary stream of cells that emerge from the alkaline submarine mound before spreading into the ocean floor sediments and lavas of the early Earth to produce the first subsurface biosphere (Reysenbach and Shock, 2002).

So life quickens by many orders of magnitude, reactions that would go anyway, though generally at an infinitesimal pace. The real entropic output of life then is not the complex organic molecules that constitute living cells and enable the processing, but those waste products closer to equilibrium than the reactants, such as methane, acetate and certain sulfides and oxides as well as the recalcitrant stable organic molecules such as the hydrocarbons that tend to be interred within the sedimentary piles. That is not to say that methane and acetate can't in their turn be used as energy and material sources—merely that they have lower energies than the original feedstocks. Knowing why life emerges, and how it plays out its role, informs us how to plan its detection on other terraqueous worlds both near and far.

2. WHY DOES LIFE START?

The biosphere, the collective zone of all life, was the last sphere to differentiate on our planet. Prior to the onset of life, the differentiation of core, mantle, asthenosphere, lithosphere, and volatisphere (i.e., hydrosphere and atmosphere) was largely a response to radiogenic and gravitational heat production in the interior. One effect of this was to gather electrons in the core in native iron (Fe^0 with its full electron complement). However, early core formation still left the upper mantle relatively electron-rich (mainly in Fe^{II}-bearing minerals). In contrast the exhaling and accreting molecular volatiles (H_2O, CO_2, N_2, NO, SO_2, P_4O_{10}) that composed the early volatisphere were highly oxidized (Albarade, 2009) (Fig. 1). Yet apart from the polyphosphate, these volatiles are susceptible to reduction at lower temperatures when brought into contact with the relatively electron-rich crust: to hydrogen, methane, ammonia and sulfide. In particular, Everett Shock (1992) has shown that while the major phase of carbon is carbon dioxide (or carbonate) at temperatures greater than 400°C—and certainly at all volcanic temperatures—as temperatures of interaction between the outer lithosphere and CO_2 drop below ~400°C, then methane becomes the thermodynamically stable phase of carbon (Fig. 2). However, because of kinetic barriers, CO_2 remains metastable, and only a small proportion tends to be reduced to methane on interaction with the ferrous iron rich crust, notably during the process of serpentinization. Serpentinization is the exothermic hydration, carbonation and oxidation of ultramafic rocks and is the key to the emergence of life (Russell et al., 1989). In this process, much of the ferrous iron within the fayalite (Fe_2SiO_4) portion of olivine comprising this ocean crust is eventually oxidized to magnetite (Fe_3O_4), while concomitantly some water is reduced to hydrogen, and the carbon dioxide is then hydrogenated to methane (and water) (Proskurowski et al., 2008; Klein et al., 2009). At the Lost City exhalative site in the North Atlantic up to 2 mmol/kg of methane is registered along with up to 14 mmol of unspent hydrogen. In other words, electrons are transferred, albeit tardily, from the ferrous iron in the oceanic crust to these reduced volatiles that then carry them toward the surface—toward the electron poor volatisphere.

Given the tardiness of reaction we might expect some partially reduced carbon-bearing molecules also to be generated during serpentinization, such as formate ($HCOO^-$) and, perhaps, acetate (CH_3COO^-). While some abiotic formate has been noted at certain hot springs of moderate temperature, the more complex acetate molecule, metastably poised between being fully oxidized and fully reduced, is found only in micromolar amounts; amounts which anyway may well be of biotic origin (Lang et al., 2009). Acetate production appears to be a prerogative of life. Indeed, if carbon dioxide were more susceptible to reduction to methane

and acetate there would be no call for life in the universe. It is the very stability of the carbon dioxide molecule that has led to the subtle catalytic and energy-gathering processes of anaerobic life. And without anaerobic life there could have been no evolution to photosynthesis, nor to multicellular organisms. Life emerges as a thermodynamically driven attempt to quicken particular thermodynamically-challenged reductions, achieving metabolic networks consisting of metastable organic molecules occupying the phase space delineated by Shock (1992) (Fig. 2)—but how?
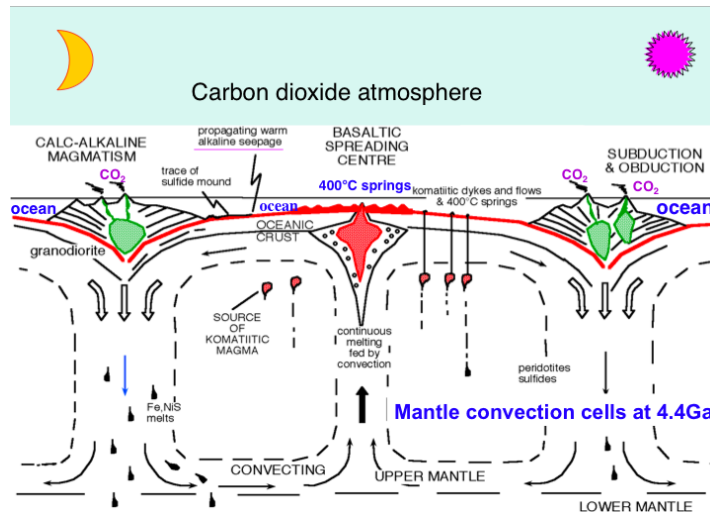

Figure 1. Cross-section of mantle convection cell assumed for the Earth at 4.4 to 4.3 Ga (Holmes, 1931; Macleod et al., 1994). Convection leads to the differentiation of various spheres, e.g., the mantle, lithosphere (including the oceanic crust), and the hydrosphere and atmosphere. Note the warm (≤90°C) alkaline seepage, one of many in the deep ocean at which the putative silicate/ hydroxide/ carbonate/ sulfide mounds developed and life emerged within the zone of metastable organic molecules pictured in Fig. 2.
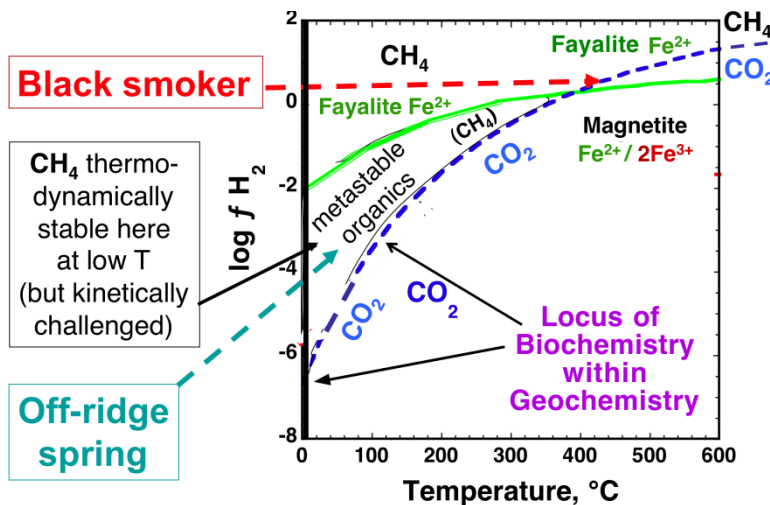

Figure 2. Plot of the log of H_2 fugacity (fH_2) against temperature. Solid curves show the 0 contour of log fH_2 buffered by the quartz-magnetite-fayalite (SiO_2-$Fe^{II}Fe^{III}_2O_4$-$Fe^{II}_2SiO_4$) mineral assemblage as a function of temperature. The green corresponds to a contour of log (fCO_2/fCH_4) equal to 0 also as a function of temperature. The two curves crossover around 400°C. CO_2 reduction to CH_4 becomes progressively more kinetically

inhibited as temperatures drop beneath this value. The broad region between CO_2 and CH_4 where organic molecules in various redox states are metastable is that exploited in the give-and-take of life and is the region in which life emerged, probably at an alkaline spring between 40° and 100°C. In the absence of life and its well-poised redox enzymes only CO_2, CH_4, some higher hydrocarbons and formate (an intermediate on the geochemical path to methane) appear to occur (Lang et al., 2009). CO_2 is stable in mafic and ultramafic magmas and is constantly delivered and returned to the atmosphere through volcanoes. Redrawn from Shock (1992, fig. 17).

3. HOW DID LIFE EMERGE?

The kinetic barrier to a fuller hydrogenation of carbon dioxide is responsible for the complexity of life. And it is the initial steps in the hydrogenation pathways that provide the challenge. The lack of success in producing even the simplest of molecules in the laboratory, such as formate, formaldehyde and acetate from carbon dioxide in conditions representing those on the early Earth, has stymied progress in origin of life theory in spite of some thermodynamic encouragement (Shock, 1992; Amend and McCollom, 2009). Why is this? Generally it is the physical tensions that have been ignored in the endeavor to reproduce these, the most challenging first steps. Chemical energy is not sufficient to mount the thermodynamic barriers to the synthesis of these first (and simplest) organic molecules. Clearly we have to get the physics right before we tackle the chemistry. And of course, any theory has to make evolutionary sense—electrochemical energy is needed in the range commensurate with that employed by metabolism as we know it today. What would be the source of such energies and how could they be spent to drive life into being?

The answer we believe is summed up in the term chemiosmosis. This concept, introduced by Mitchell in 1967, explains how redox energies are used in all life today to pump protons out of the cell, that they might return through a highly evolved rotor-stator motor to generate adenosine triphosphate (ATP) from the di- or mono-phosphate, the energy currency of life (Harold, 1986). ATP drives condensations and polymerizations. Clearly such a mechanism, and such a molecule, could not just materialize fully-fledged at the hot spring (Fig. 3). But reference to the initial conditions tells us that such a complex mechanism to pump protons to the exterior of a cell or compartment would not be required at life's emergence. The protons were already dammed up there, outside in the carbonic ocean bathing the hydrothermal mound (Fig. 4). They merely had to be tapped through a compartment wall to drive the generation of inorganic triphosphate, which in turn could drive proto-biosynthetic reactions like condensations and polymerizations (Russell and Hall, 1997, 2006). The ordinary, inorganic phosphate derived from volcanic gases would do in place of adenine phosphates (Yamagata et al., 1991; Russell et al., 1994; Hagan et al. 2006).
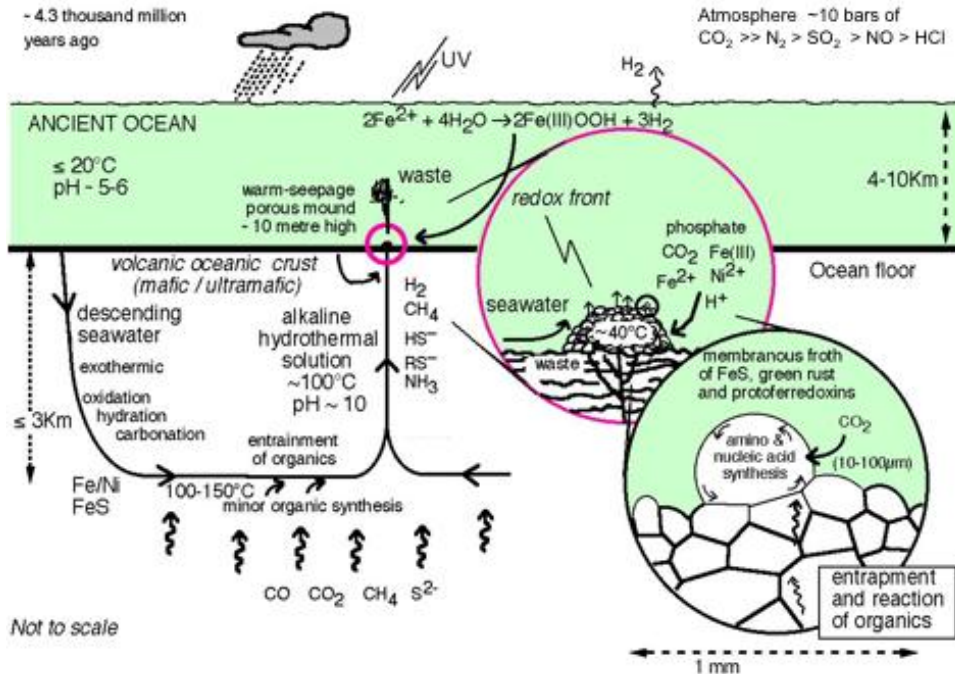
Figure 3. Model environment for the emergence of life at a submarine alkaline ~50°C seepage on the floor of the earliest ocean comprising a silicate-carbonate-hydroxide-sulfide mound (Russell and Hall, 1997).

Reductions could also have been driven by another chemiosmotic mechanism. We have seen that carbon dioxide (O=C=O) is a stable molecule that resists hydrogenation, even though hydrogen is concentrated in the alkaline hydrothermal solution. However, nitric oxide, or nitrate and ferric iron would also be present in the ocean bathing the mound (Cairns-Smith et al., 1992; Martin et al., 2007), and these entities would be much more eager to accept one of the two electrons orbitalling the hydrogen molecule (Ducluzeau et al., 2009) (Fig. 5). This is where one or other of the vital VIB elements come into play, molybdenum or tungsten: elements delivered in the alkaline hydrothermal solution (Russell and Hall, 1997). Stable oxidation states of both elements are either 4+ or 6+. Were Mo^{4+} to lose an electron to nitrate or ferric iron, then the second electron would be that much more energetic, and would have the power to reduce CO_2 to formate (HCOO⁻) (Nitschke and Russell, 2009) (Fig. 5). Thence the formate could be hydrogenated with the involvement of the protonmotive force:

$$HCOO^- + H_2 + H^+ \rightarrow HCHO + H_2O.$$
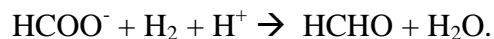
From the resulting formaldehyde the remaining hydrogenations or carboxylations are downhill to either methane or acetate, and on to other carboxylic acids (Morowitz et al., 2000). Note that while we talk of these molecules and ions as separate entities, they will be chelated either to metals and metal sulfide clusters or other organic molecules. Indeed, it is

7

apparent that several of the d-block elements are vital to life, both at its emergence, and at the onset of oxygenic photosynthesis (Table 1). Indeed, to borrow a phrase from David Garner, "it is the inorganic elements that bring organic chemistry to life".
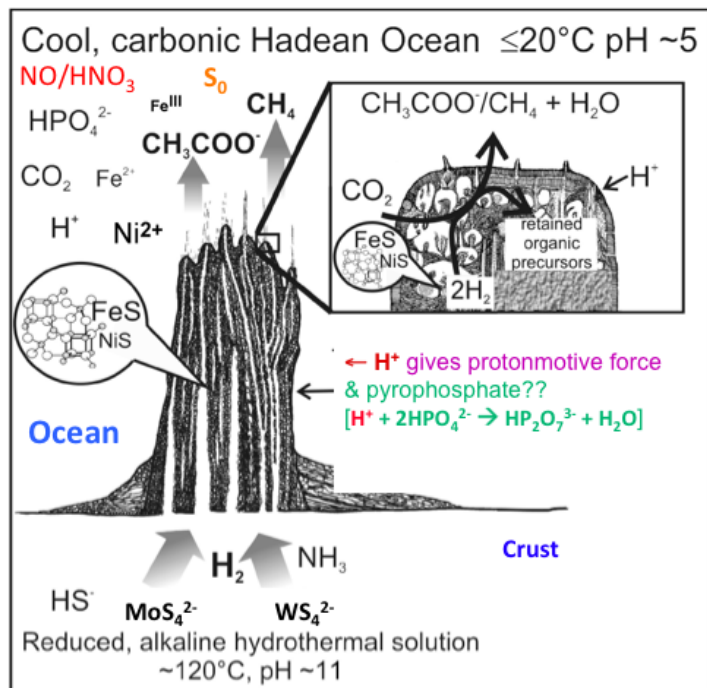

Fig. 4. The hydrothermal mound growing above a submarine alkaline seepage acts as a natural self-restoring flow reactor and fractionation column. The walls of the complex three-dimensional semiconducting and semipermeable inorganic compartments comprising parts of the mound and occupied by the flux of alkaline, hydrogen-bearing hydrothermal solution, comprise catalytic nanocrysts of iron sulphides dosed with other metals. The sulfides and hydroxides are interspersed with amorphous silica, silicates and ephemeral carbonate. The ambient pH and redox gradients imposed on the outer margins of the mound drive life into existence. After Russell and Martin (2004), Nitschke and Russell (2009) and Mielke, McGlynn and Robinson (in prep).
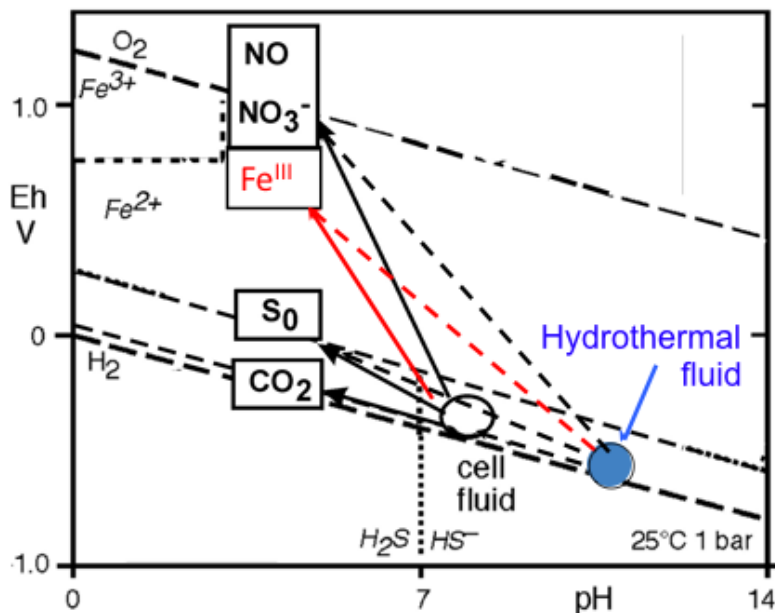
Figure 5. Redox potential/pH vectors between the formative alkaline hydrothermal fluid (as well as of the cellular fluid of the ensuing prokaryotes) and that of the Hadean oceanic environment represented by electron acceptors. After Russell and Hall (1997).

Once carboxylic acids have been produced in the alkaline conditions obtaining in the mound they will be ripe for amination to amino acids. Huber and Wächtershäuser (2003) have achieved such aminations at high yield in the presence of FeS or $Fe(OH)_2$ as catalyst. Rabinowitz et al. (1969) and Rabinowitz and Hampaï (1985) had previously shown how amino acids could be condensed with trimetaphosphate to di- and tripeptides, also in alkaline conditions. And once short peptides are available in the mound they will sequester inorganic ions, either directly as with the metallic ions Co^{2+} and Ni^{2+} (Martin et al., 1960; Alipázaga et al., 2004) or indirectly through hydrogen bonding to anionic entities such as metal sulfides and the ortho- and trimetaphosphates. Milner-White and Russell (2005, 2008) have characterized the active centers as 'eggs' and the short peptides ensconcing them as 'nests' (Table 1). These short peptides would be an improvement on the merely inorganic components of the first metabolizing compartments (McGlynn et al., 2009) and it is possible that longer peptides took over the structural job of acting as the first cell walls and membranes while still retaining their propensity to sequester the active inorganic clusters (Milner-White and Russell, 2008).

Table 1. Metal-assisted metabolism: metal complexes either grew to the size of clusters and beyond that, to minerals in the hydrothermal mound, or instead were sequestered by either the amine groups of short peptides or their carboxylates to comprise protoenzymes (Milner-White and Russell, 2005, 2008).

MINERAL	←COMPLEX→	ENZYME CLUSTER	CHELATOR
Kanonerovite $MnNa_3P_3O_{10}.12H_2O$	$HPO_4^{2-} + HP_2O_7^{3-} + 2H^+ \rightarrow H_2P_3O_{10}^{3-} + H_2O$	trimetaphosphate $H_3P_3O_{10}^{2-}$	Successive main chain NH^+ peptide nests
Mackinawite (Fe>>Ni)S	$[FeS_2Fe]4H_2O$ $[FeS_2Ni]4H_2O$	(Rieske protein) Hydrogenase e^-	Thiolated egg in peptide nests?
Greigite cuboidal moiety	$2[FeS_2Fe]$ $\rightarrow [Fe_4S_4]^{2+} + 2e^-$	Ferredoxins $[Fe_4S_4]^{0/+}$, $[Fe_3S_4]^{+/2+}$	Thiolated egg in peptide nests?
Greigite as $NiS_2[Fe_4S_4]S_2Fe$	$NiFe_5S_8$	CODH/ACS $NiFe_4S_5$ & $[Fe_4S_4]cys$-Ni-cys_2-Ni	Ni-peptide & thiolated egg in peptide nests
Greigite twin as $[Fe_4S_3]S_4[S_3Fe_4]$	$[Fe_4S_4]^{2+/+}$ & MoS_4^{2-}	Nitrogenase $[Fe_4S_3]NS_3[S_3Fe_3Mo]$	Peptide nests + carboxyl group?
Hollandite or tunnel manganite	$Ba(Mn^{4+},Mn^{2+})_8O_{16}$ or $CaMn_4O_8$	O_2 evolving complex $MnCaMn_3O_5(aa)_8$ $\pm 2H_2O$	Periplasmic carboxyl groups

The sequences of reductions that first led to acetate (and thence to the carboxylic acids) are the most straightforward and constitute what is known in biochemistry as the acetyl coenzyme-A pathway, considered by Fuchs (1989) to be the most ancient of the pathways and cycles. The very first proto-organism to beat this metabolic pathway was likely an acetogen, i.e., it produced acetate as a waste product of biosynthesis in an energy-generating process known as substrate phosphorylation (Fig. 6) (Russell and Martin, 2004). Although methanogenesis uses the same path, the way some of the energy is garnered is extremely complex and involves many more enzymes and proteins (Fig. 7) (Grabarse et al., 2001). Thus methanogenesis is likely a later evolutionary development, though both acetogenesis and methanogenesis probably operated in the mainly inorganic compartments comprising the hydrothermal mound before the cellular diaspora (Martin and Russell, 2007). Indeed, the acetogens were probably the forerunners of the bacteria and the methanogens the forerunners of the archaea, the two domains of the prokaryotes (Martin and Russell, 2007). Both processes are assumed to have operated in the last universal common ancestor of all life: the LUCA (Martin and Russell, 2007). And as we might expect from this evolutionary sequence of metabolic pathway, the methanogens can also grow on acetate, notably in the deep biosphere (Buckel, 1999; Heuer et al., 2009).
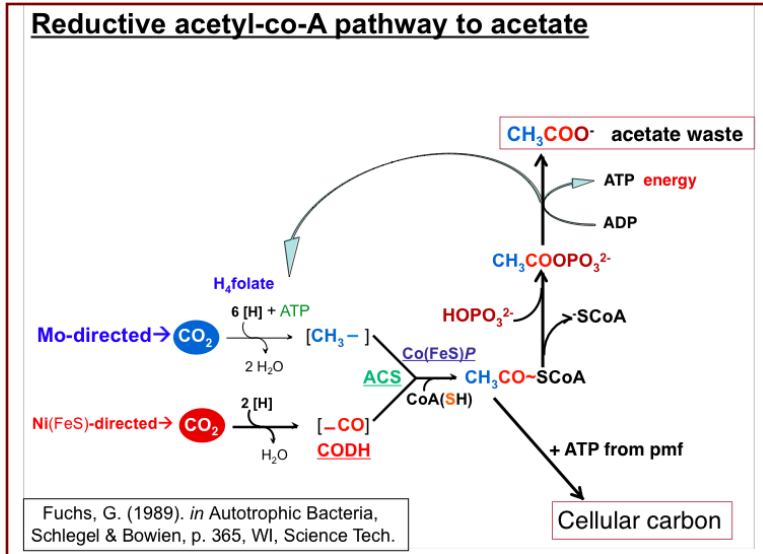
Figure 6. The acetyl coenzyme-A pathway as employed by the acetogens. It produces both biochemical components and some energy in the form of adenosine triphosphate (ATP) (Fuchs, 1989). The acetogens are assumed here to have been the first microbes. Carbon monoxide dehydrogenase/acetyl coenzyme-A synthetase (CODH/ACS) is the bifunctional enzyme wherein one nickel is involved in the reduction of CO_2 and another nickel is involved in synthesizing the acetyl group (Volbeda and Fontecilla-Camps, 2006).
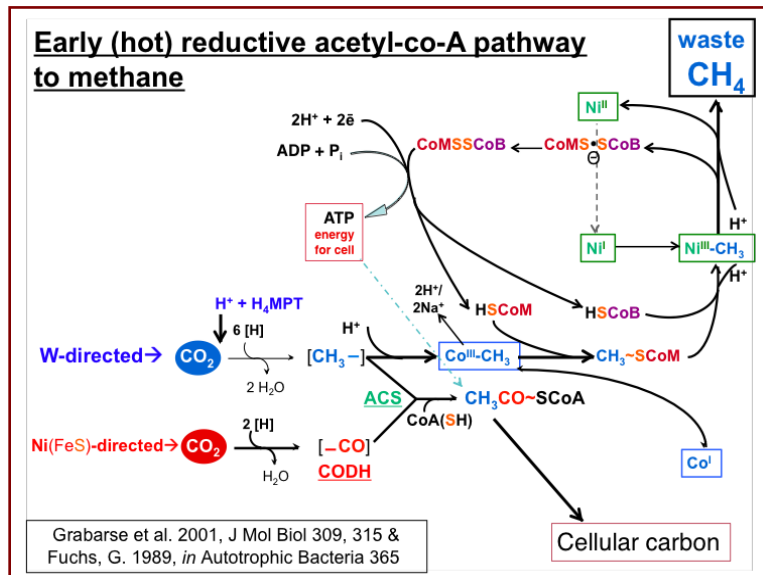

Figure 7. The acetyl coenzyme-A pathway as employed by the methanogens. The energy-extracting process is much more complicated than that of the acetogens (Fig. 6) and thereby is deemed to be a later evolutionary invention. It involves the transfer of the methyl group from coenzyme-M to produce CH_3-Ni^{III}-F_{430} which then oxidizes CoM to the thiyl radical as it is reduced to CH_3-Ni^{II}-F_{430}. F_{430} is protonolysed to methane while the CoM thiyl forms a heterodisulfide radical with coenzyme-B thiolate. The heterodisulfide is rehydrogenated in a reaction that only then produces energy in the form of ATP (Fuchs, 1989; Grabarse et al., 2001).

Here we have attempted to explain how the first vehicles of metabolism were generated and how they were energized and how their cell walls may have evolved from mineral beginnings to peptidic compartments while still retaining their capability of sequestering the active inorganic small clusters and ions. What is missing of course is how they may have complexified and evolved. For this the metabolizing vehicles required regulators and a code for their offspring. This genetic code was probably pieced together from coenzymes such as ATP that already had jobs to do in energy transfer and catalysis (White, 1976). How the code itself first operated has been considered most recently by Mellersh and Wilkinson (2000), Copley et al. (2005) and Yarus (2009), while Koonin and Martin (2005) show how it may have evolved in the form of retroviruses permeating the hydrothermal mound.

4. WHAT DOES LIFE DO?

There have been hundreds, perhaps thousands, of attempts to answer the seemingly profound question 'what is life?' Yet still the query is batted around with no concern for earlier speculations and no widely agreed definition. How much more revealing is the question 'what does life do'? At the thermodynamic level it evolves to maximize entropy and attempts to reach this state as rapidly as possible (Kleidon and Lorenz, 2005). It thereby augments energy-dissipation as mediated by convective processes to which it is coupled. From a mechanistic point of view life (partially) hydrogenates carbon dioxide in the atmosphere or dissolved in the hydrosphere. In the beginning a small but continuous supply of organic molecules is produced with most of the electrons ultimately derived through the oxidation of iron residing in the crust and mantle. Acetate, then methane, were produced as waste entities in the process. For this to happen probably required electron acceptors and certainly also metals in the active centers of many proteins (Table 1). Indispensible to life at least as we know it are Fe, Zn, Ni, Co, Mo, W, V, Cu, Mn, Ca and Mg (Zerkel et al., 2005). The first electron acceptors were CO_2 and NO or their hydrolyzed equivalents, and colloidal ferric iron (Russell and Hall, 1997, 2006; Ducluzeau et al., 2009) (Fig. 5). Once life had departed the original mound then sulfur oxides, manganese oxides and sulfur itself came to be exploited. For example, sulfate reduction, which is strongly endergonic and requires 3 ATP molecules and two electrons to be reduced to sulfite, was clearly post-LUCA (Fuchs, 1999). Sulfate was first exploited by the archaea and the mechanism purloined by the bacteria through horizontal gene transfer (Klein et al., 2001).

Once motile, or at least prone to dispersion via convection currents of various types, life evolves as a search engine for energies and materials

commensurate with its optimal or near optimal functioning conditions. Energy was first gleaned from the geochemical disequilibria on this wet rocky planet before the appropriate energies from the sun were mastered (Table 1). The use of photons as an energy source required that the high energy deleterious wavelengths be masked, first adventitiously by mineral particles (Phoenix et al., 2001) and then by cyclic organic compounds, originally produced as components for electron transfer (Eschenmoser, 1988; Pratt, 1993). Some of these ring compounds were turned to good use as antennae, whereby longer wavelength solar radiation was used to prize electrons from the ligands surrounding the nuclei of magnesium (Mulkidjanian and Junge, 1997).

Eventually oxygenic photosynthesis emerges, and water is reduced through the action of photons for the much more effective hydrogenation of carbon dioxide (Baymann et al., 2001; Allen, 2005). For this to happen required yet another naturally occurring mineral cluster, this time comprised of a $CaMn_4$ molecule (Sauer and Yachandra, 2002; Yano et al., 2006; Russell et al., 2008; Guskov et al., 2009). In this case oxygen is the waste volatile which, after oxidizing proximal reduced molecules, is then released to the atmosphere (Rosing and Frei, 2004; Buick, 2008) (Fig. 8, Table 2). While oxygen was a challenge to anaerobic microbes (Lane, 2002), once mastered by a few as an electron acceptor, then life really began to burgeon (Rosing, 2005; Sleep and Bird, 2008). The question, has emerged life, and if so how far has it evolved on other terraqueous worlds, is the goal of life detection methods.
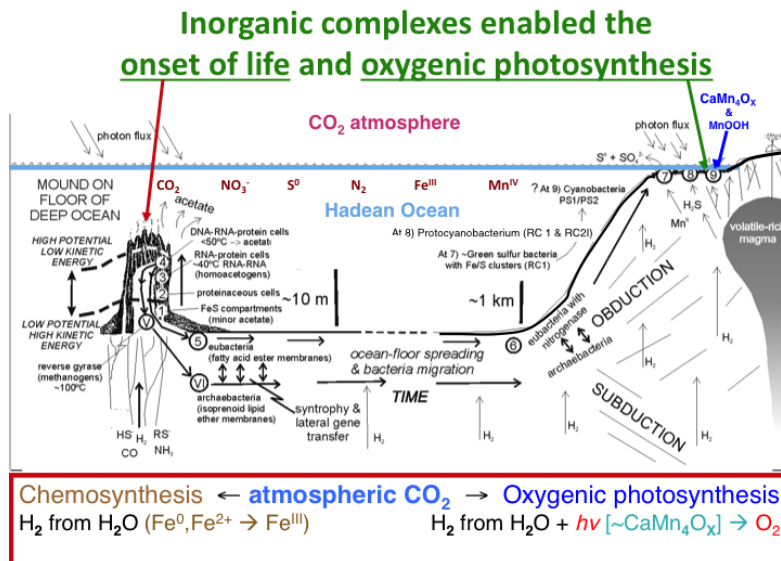

Figure 8. Chemosynthetic life emerged at a warm alkaline seepage at the bottom of the Earth's early ocean before differentiating into the precursors of the Bacteria and Archaea. Thereafter it expands downwards and laterally into and onto the surrounding sediments and crust. From there a proportion is conveyed by ocean floor spreading toward a constructive margin produced by overthrusting (obduction). Once uplifted at the margin, some of the cells happen to invade sediments in the photic zone where, at a sulfurous

spring, some evolve to exploit solar photons. Numbers 1–3 relate to life's emergence, and 4 marks the point of differentiation of the Archaea from the Bacteria. Roman numerals V and VI mark evolutionary stages of the Archaea, and 5 and 6 indicate stages of evolution of the Bacteria in the deep biosphere. Photon energy was first mastered by the green sulfur bacteria (7), followed by the heliobacteria (8). These photosynthesizing bacteria had appeared at least by the early Archaean (Allwood et al., 2009). Oxygenic photosynthesis (9) is a further development that may have evolved at a manganiferous hot spring by 3.75 Ga (Russell et al., 2008). (Various scales.) (After Russell and Arndt, 2005).

Table 2. Evolutionary sequence of carbon dioxide fixation. Abiotic serpentinization predates the more efficient anaerobic acetogenesis, methanogenesis and sulfate reduction. Oxygenic photosynthesis is more than an order of magnitude more efficient still.

CO$_2$ hydrogenation mechanisms quicken, complexify and evolve on rocky, wet, icy worlds

1. Serpentinization (redox and heat) → some CH$_4$

----------------------------------*life emerges*--------------------------------

2. Bacterial acetogenesis (H$_2$, pmf, PPi) → CH$_3$COO$^-$

3. Archae-methanogenesis (H$_2$, pmf, Co-B, Co-M, PPi) → much CH$_4$

4. Archaeal then bacterial sulfate reduction (H$_2$) → H$_2$S + CH$_3$COO$^-$

5. Bacterial oxygenic photosynthesis (photons, CaMn$_4$O$_x$) → O$_2$

5. WHERE WILL IT BE?

We begin this section by considering where life could not occur, for the first rule of prospecting is to identify barren terrains. Lewis and Prinn (1980) argue that in our solar system kinetic inhibition of CO and N$_2$ reduction was so slow relative to radial mixing as a whole that it remained relatively oxidized. Thus, close into our own sun though the rocky planets were high temperature condensates, beyond Venus they are cool enough to retain water as well as carbon dioxide and thereby possibly harbor life (Pavlov et al., 2005; Valley et al., 2006). We have learnt to our surprise that our solar system does not appear typical. So far, many appear to

comprise massive gas giants close in to their star, presumably having mopped up any terraqueous planets during inward migration (Bond et al., 2009). Moreover, planets around pulsars and white dwarfs and toward the galactic center, and even similar system to ours, could if their C:O ratios exceeded unity (i.e., only a factor of 2 more than in our own solar system), be composed of silicon carbide and graphite rather than silicates and be quite dry (Esteban et al., 2005; Kuchner and Seager, 2005). Without water, that universal solvent, and in the consequent absence of resolvable geochemical tensions there would be no call for life (Larimer, 1975). Similarly, hydrogen, helium, nitrogen and iron planets will not differentiate to the extent of producing electrochemical tensions commensurate with biochemical reactions.

Wet, silicate planets probably only occur circling third and fourth sequence stars and those that are likely to harbor life would necessarily be born from high metallicity and oxygen-rich protoplanetary discs. High metallicity is important because life is extraordinarily dependent on transition elements (da Silva and Williams, 2001; Zerkle and House, 2005). For example, it is possible that the element with atomic number 74, tungsten, may have been required not merely for hyperthermophilic methanogenesis, but for the very origin of the Archaea, the other prokaryotic domain. And, judging from our knowledge of this planet, without an autotrophic archaeal host there could have been no complex life, for nucleated cells were born of the endosymbiotic adsorption of a heterotrophic bacterium (Martin and Russell, 2003, fig. 7).

After ruling out so many solar systems, still we argue that life will be common in the Universe give the right initial conditions. Rocky planets large enough to have retained a volatisphere can be expected to have hot interiors, especially when young. Reasons are gravitational and tidal potentials as well as radiogenic heat. We don't have to go to them to know that convective mass transfer will onset in their various spheres depending on thermal gradients, radius, viscosity and, in the wet crust, permeability. Life is likely to have a not dissimilar distribution, driven by the chemical tensions resulting from those same convection currents. Planets hot enough to produce volcanoes will produce and retain a carbon dioxide and nitrogen atmosphere, probably augmented with cometary volatiles (Albarede, 2009; Bond et al., 2009). Smaller, colder worlds may have such an inventory derived entirely from meteorites and comets (Hand et al., 2007). We have seen that metabolism exists to reduce the tension between atmospheric carbon dioxide and hydrogen from a variety of sources and in various guises, just as convection exists to lower the thermal gradients across the sequence of broadly spherical shells that comprise a planet (Fig. 1).

That carbon dioxide will feature in the atmospheres and /or hydrospheres of icy as well as water worlds is because it is stable in relation to silicate magmas even in the presence of graphite (Wood et al., 1990; Hirschmann and Withers, 2008). Thus it will be the main gas exhaled from magmatically-sourced volcanoes at least in our solar system. And anyway, reduced carbon-bearing molecules emanating from the rocky interiors will tend to be rapidly photo-oxidized, especially on an icy surface (Walker, 1885; Hodyss et al., 2009). However, CO_2 will be generally out of equilibrium with the rocky crusts of wet planets which will comprise ferrous iron-bearing minerals and disseminated crystallites of native iron. Calcium-bearing pyroxenes and feldspars will tend to drawdown CO_2 through calcium carbonate formation, especially in the cold feeders to hydrothermal convection cells (Griffith and Shock, 1995). But at the same time a portion of the CO_2 in ground waters will be partially reduced to hydrogen, the fuel for partially hydrogenating carbon dioxide—a process that may lead to the emergence of life. Recognizing the drive to life's emergence on this planet has led to conclusions regarding the likelihood of its onset on other water or icy worlds.

5.1. Potentially Habitable Environments in the Solar System.

Looking beyond Earth, four bodies in the solar system, Mars, Europa, Enceladus and Titan remain the most promising sites for further elucidating concepts about chemical evolution and the origin of life. In these bodies, liquid water may persist to the present (Lyons et al., 2005; Zimmer et al., 2000; Kerr, 2005; Spohn and Schubert, 2003; Tobie et al., 2005a), raising the question of whether these planets host active hydrothermal systems similar to those found in Earth's oceans and whether other planets may have also done so in earlier epochs. Organic analyses of the surface and atmosphere will be of pivotal importance in the exploration of these bodies. The search for biologically essential elements and organic compounds will be an important task for the various missions to Mars, Europa, Enceladus and Titan that are anticipated over the next few decades by the major space agencies such as NASA and the European Space Agency. In recent years, exploration strategies have been developed to pursue astrobiological objectives for these targets such as determining the abundance and distribution of the biologically essential elements and organic compounds, detecting evidence of ancient biota and determining whether indigenous organisms currently exist anywhere on the planet. State-of-the-art analytical detection techniques with very high sensitivity will play a major role in these endeavors. Finding evidence of extinct life on one of these targeted bodies would be, to put it mildly, sensational. The presence of extant life could be even more so and would add a fresh perspective to our understanding of the chemistry of life.

5.1.1. Mars. The earliest observations of Mars by spacecraft such as NASA's *Mariner* and *Viking* missions showed that water had caused substantial erosion of the surface (Carr, 1996). More recently, NASA's Mars Exploration Rover (MER) *Opportunity* revealed that, in Terra Meridiani, sulfates must have formed in the presence of liquid water (Squyres, 2004). This endorses the interpretation from data collected by the Thermal Emission Spectrometer (TES) on-board NASA's *Mars* Global Surveyor (MGS) orbiter, which found grey hematite in a few locations—also suggestive of aqueous processes and oxidizing conditions (Christensen et al., 2001a). However, global results from TES suggest that Mars was most likely cold and dry over most of its history (Christensen et al., 2001b). Recent data from the OMEGA instrument on ESA's Mars Express, combined with MER and MGS data, has allowed Bibring et al. (2006) to postulate an aqueous history of Mars and its crustal evolution. They conclude that Mars started out relatively wet and temperate but a major climate shift occurred early in its history which led to the cold, dry place strewn with "acidic" alteration products that we see today. Their analysis indicates three sequential eras characterized by surface alteration products:- (i) *Phyllosian era* characterized by aqueous, though non-acidic alteration revealed by phyllosilicates; (ii) Theiikian era characterized by an acidic aqueous alteration evidenced by sulfates; and (iii) *Siderikian era*, a long period of atmospheric aqueous-free alteration, as indicated by ferric oxides. We consider that it is during the alkaline, moist *Phyllosian era* that life was most likely to have emerged on this planet (Shock, 1997; Russell and Hall, 1999).

Many evolutionary innovations occurred more than once on Earth, suggesting that evolutionary histories are predictable and replicable at the scale of functional roles and directions of adaptive change (Vermeij, 2006). It follows that stages in the emergence of life should be similar on all wet, rocky planets (like early Mars), at least in our portion of the Universe (Shock, 1997). Not only that, but key stages on the path to life may be reproducible in a laboratory. Given the appropriate initial conditions—in our view, a submarine and alkaline hydrothermal seepage converging and interacting with bicarbonate in an early ocean—the only randomness, chance or accident to occur during emergence would be in the chirality of molecules participating in coding and metabolism (Russell, 2007).

What evidence is there that Mars harbored deep (high-pressure), oceanic hydrothermal vents? The evidence of past geothermal activity (shield volcanoes, patera structures, lava plains) has been clear since the *Mariner* and Viking missions (Greeley and Spudis, 1981). And good evidence for hydrothermal activity has been advanced by Allen and Oehler (2008) as revealed by Mars Reconnaissance Orbiter. For large, deep bodies of water, an assortment of geologic and geochemical evidence points toward the

previous existence of wide oceans over the Martian northern lowlands. As summarized by Farién et al. (2003), these include: (1) the Martian dichotomy boundary between the southern highlands and the northern lowlands (Tanaka et al., 1992) that provides a topographically lower area in the plains for very deep water accumulation, (2) evidence of long-wavelength undulations of shorelines around the putative ocean caused by stresses associated with polar wandering (Sotin et al., 2003; Fairén et al., 2003; Perron et al., 2007); (3) the outflow channels, which either terminate at the boundary (Parker et al., 1993) or fade into the northern plains (Ivanov and Head, 2001); (4) the low density of superposed impact craters in the northern plains relative to the densely cratered southern highlands (Barlow and Bradley, 1990); (5) extremely flat topography at the distal reaches of the outflow channel systems in the northern lowlands (Head et al., 1999); (6) the broad occurrence of wide age-ranging glaciers that are interpreted to be linked to magmatic-triggered flooding and associated short-lived (tens of thousands of years) environmental/climatic changes (Cabrol et al., 2001); and (7) the chemical signatures reported for the northern plains, including high abundances of S and Cl or the possible existence of sulphate minerals and chloride salts, making a putative andesite-rich component or weathered basalt the dominant material type in the lowlands (Wyatt and McSween, 2002; Bibring et al., 2006).

Taken together, the above lines of evidence is best explained by a large standing body(ies) of water. In order to achieve a water pressure of 100 psi, a Martian ocean would only need to be about 186 m deep (100 psi = about 7 bars, which on Earth would need an ocean/lake about 70 meter depth so on Mars divide by 0.38 = 186 m). This value is easily exceeded if the northern ocean were to have been 1800 meters deep (Head et al., 1999) or 1500 m deep (Parker et al, 1993).

5.1.2. Europa. Jupiter's moon Europa, like other icy satellites, lies outside the so-called Habitable Zone—the solar orbital region in which surface liquid water is stable under the Sun's heat. However, tidal heat input to Europa's interior is, in theory, sufficient to support some amount of liquid water beneath the moon's icy surface (O'Brien et al., 2002). Heat from the decay of mantle radionuclides, and potentially also from hydration of olivine (serpentinization; Vance et al., 2007), may aid in sustaining liquid beneath Europa's surface, and beneath the surfaces of other icy satellites depending on the conditions of their formation (e.g., Matson et al., 2007; McKinnon and Zolensky, 2003). Results from the Galileo mission support the possibility of an ocean in Europa: the moon's icy surface is young (Zahnle et al., 2007) and active over geological timescales (Figueredo et al., 2003; Figueredo and Greeley, 2004) (Fig. 9, 10), and magnetometer measurements (Zimmer et al., 2000) reveal an induced field within the moon's 80-170-km thick H_2O outer layer indicative of a salt-rich ocean (Anderson et al., 1998). Cratering and tectonic features on Europa (Turtle

et al., 2001; Greenberg et al., 1998; Hoppa et al., 1999) raise the possibility of material from deep within the ice sheet having been deposited on the surface. If endogenous biosignatures are detected on the surface of Europa, they may be ultimately coupled to activity occurring at the seafloor. Tidal heat energy may drive volcanism (O'Brien et al., 2002), which is associated with chemically driven hydrothermal ecology on Earth. In the absence of vigorous tidally driven hydrothermalism, chemical activity necessary to support life may nevertheless occur at surprisingly high levels. Vance et al. (2007) showed that Europa and other small objects with lower gravity and smaller inventories of radiogenic elements will have deeper brittle uppermantle layers. As these objects cool and their internal heating diminishes their brittle layers thicken further. Over geological time, the brittle mantle layer is likely to fracture and undergo aqueous alteration. Depending on Europa's initial composition, this would mean roughly a fourfold increase over similar calculations for Earth in the per-unit-area amount of hydrogen produced by serpentinization. Though the chemistry of Europa's ocean remains uncertain, the chemistry of the Europan surface may provide clues to the subsurface.
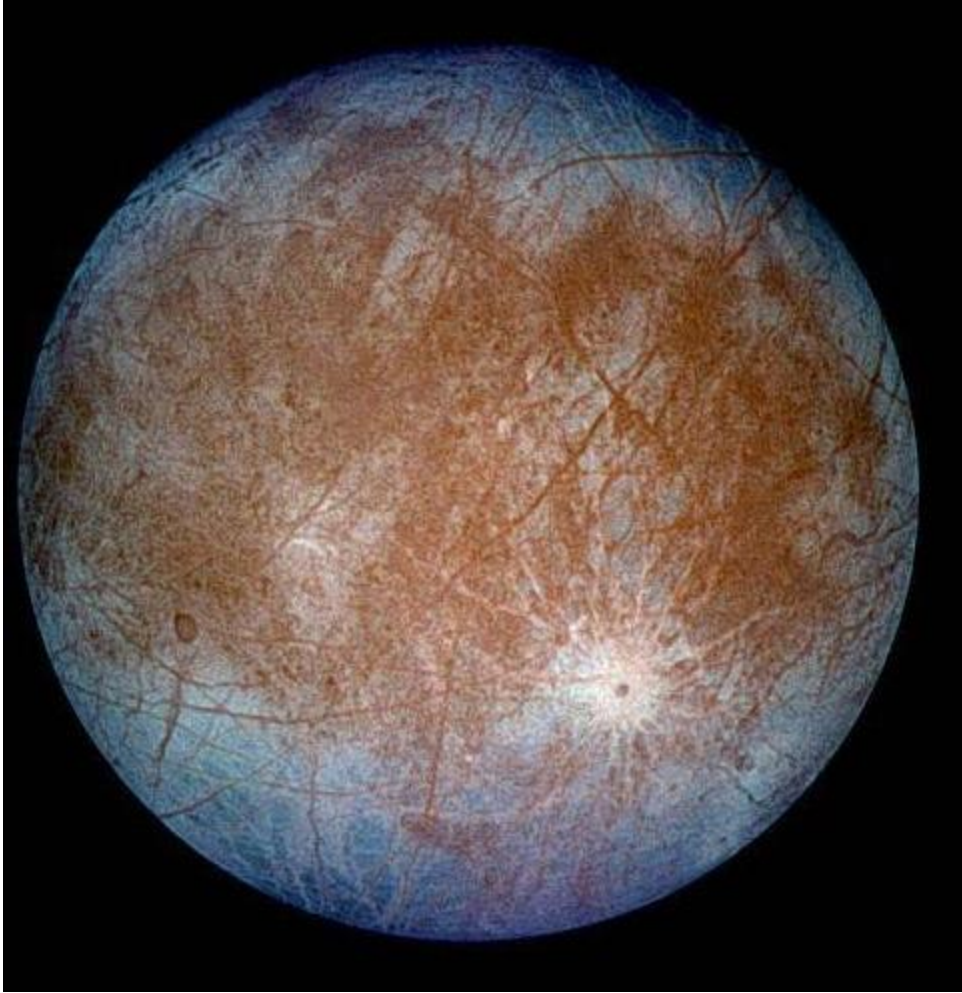
Figure 9. Europa, as seen by the *Galileo* spacecraft. Courtesy of NASA.
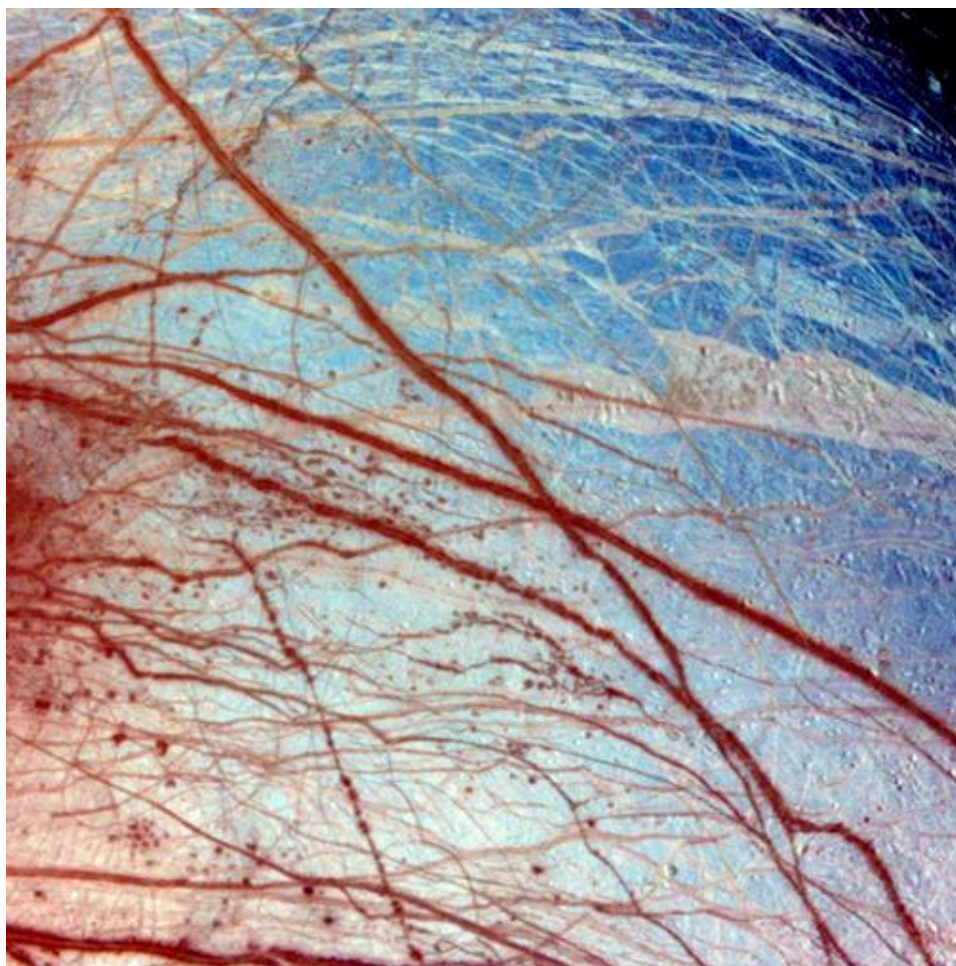
Figure 10. Europa. Close up surface features. Courtesy of NASA.

Hydrated sulfate is in great abundance on the trailing hemisphere of Europa, accounting for upwards of 90% of the surface compounds (McCord et al., 1998; Carlson et al. 2005). Carbon dioxide has also been observed on Europa and nitrile bands (C≡N) were reported for Ganymede and Callisto (McCord et al., 1997). (Spectra of Europa were too noisy to distinguish the absence or presence of the nitrile band.) In laboratory experiments replicating the radiolytic surface environment of Europa, Hand et al. (2007) showed that CO_2-rich ice processed by high-energy electrons at 100K yields a mixture of CO_2, CO, and carbonic acid. It was also shown in that work that even if surface material on Europa reaches the ocean on timescales of hundreds of millions of years, the ocean would still be rich in sulfate and carbonate ions. As such, the consideration of an alkaline origin for life is germane not just to our understanding of life here on Earth, but so too for the distant ocean of Europa (Hand et al., 2009). In the long term detailed information on potential biosignatures and on the composition of the Europan ocean will be targeted by any Europa lander (Lipps and Rieboldt, 2005). Such a mission could provide evidence that life existed or still exists near hydrothermal vents in that ocean. Important

components of such a lander would be technologies related to long-term Europa exploration goals—especially those dedicated to looking for signs of life.

5.1.3. Enceladus. The recent discovery of water vapor plumes ejected from fissures near the south pole of Saturn's satellite Enceladus (Matson et al., 2007) impels us to point out the relevance of this icy satellite to the evolution of organic molecules and possibly life in this unique physical and chemical environment (Parkinson et al., 2008). Cassini's first look at Enceladus' south pole revealed a series of approximately parallel fissures, nicknamed the "tiger stripes", that are the source of water vapor plumes propelled 80 km above the surface (Fig. 11) (Porco et al., 2006; Hansen et al., 2006). The region around the fissures has been extensively resurfaced and thermal emission from the region indicates a strong source of subsurface heating. Although the physical mechanism for production of the heat is being debated, there is no question that a significant and persistent heat source is present. Clearly, sufficient heat is present to generate the energetic flux of water vapor from the fissures and elevate the temperature of the surrounding region. Substantial subsurface temperature gradients are expected. It is possible that weathering of rocks by liquid water occurs beneath the surface. Enceladus' active hydrological cycle, where ice is heated, water vapor is expelled from the fissures, some of which coats the surface resulting in Enceladus' extraordinarily high albedo, is a unique and promising new environment in which to trace organic chemical evolution and possibilities for life. The probable presence of CO, CO_2 and N_2 suggests that embryonic formation of amino acids at any rock/liquid interfaces on Enceladus is feasible (cf. Amend and McCollom, 2009). UV photolysis results in chemistries that are highly variable depending upon trace impurities. Additionally, the large temperature gradient may be a driving force behind the generation of organic matter. The hydrological cycle on Enceladus, along with the action of energetic UV photons on water vapor, may result in continuous production of hydrogen peroxide (H_2O_2) (Hunten, 1979). Photochemically produced H_2O_2 has been suggested to drive the evolution of oxygen-mediating enzymes leading to oxygenic photosynthesis (Liang et al., 2006).
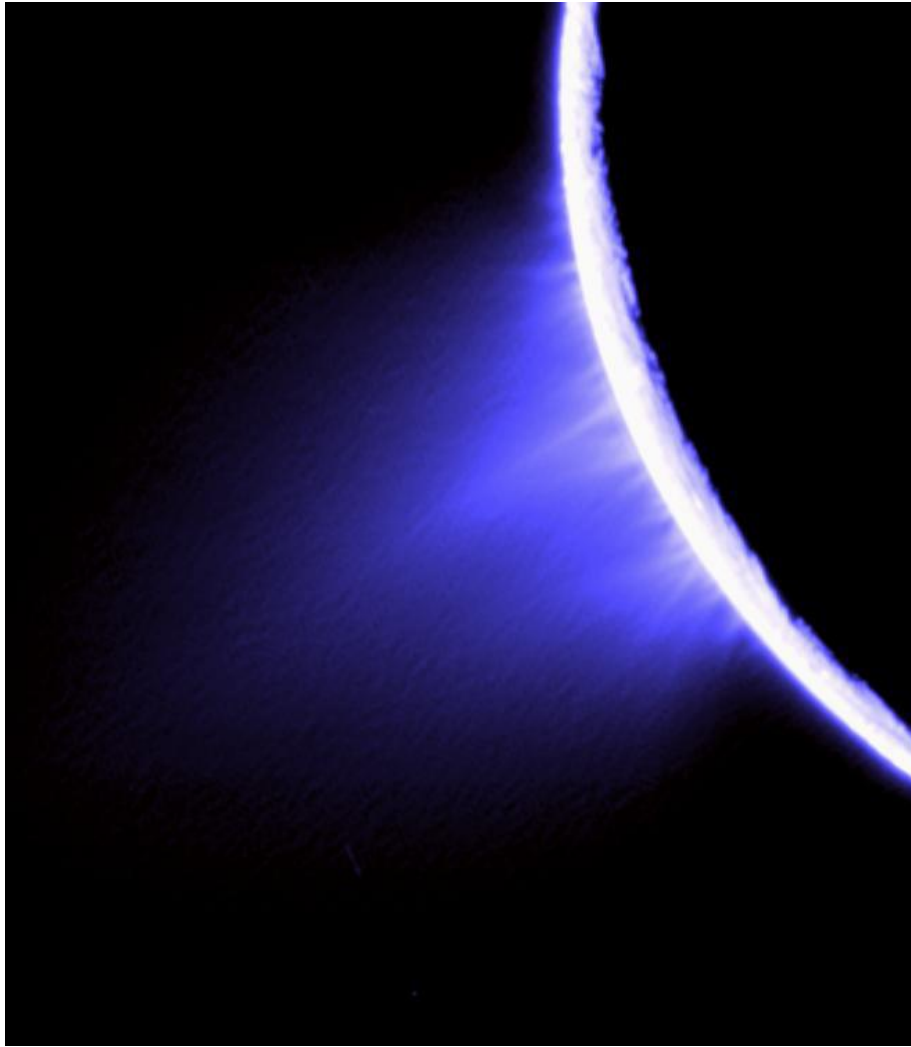
Figure 11. False-color image of jets (blue areas) in the southern hemisphere of Enceladus taken with the Cassini spacecraft narrow-angle camera on Nov. 27, 2005. The individual jets that comprise the plume may also be discerned. Credit: NASA/JPL/Space Science Institute.

As a potential cradle of life, an active hydrological cycle on Enceladus has obvious advantage over an isolated subsurface ocean sealed beneath an ice crust, like those postulated for Europa and Callisto, where without photosynthesis or contact with an oxidizing atmosphere the system will approach chemical equilibrium and annihilate ecosystems dependent on redox gradients unless there is a substantial alternative (for example, geothermal) energy source. This thermodynamic tendency imposes severe constraints on any biota that is based on chemical energy (Gaidos, et al. 1999) but would be immaterial for Enceladus.

5.1.4. Titan. Recent exciting results from Cassini have raised new questions about Titan, a moon of Saturn. Although Titan is far from the Sun, solar radiation interacts with the methane rich nitrogen atmosphere to

initiate the formation of complex organic molecules and aerosols that eventually deposit on Titan's active surface. Such a reduced volatisphere contrasts strongly with those of Mars, Europa, Enceladus and the Hadean Earth. These four bodies are comparable in the geochemistry of their outer spheres to living autotrophic cells—oxidized on the outside ($H_2O \pm CO_2$), reduced within ($Fe^{II} \rightarrow H_2$). Titan on the other hand is more like a heterotroph, or a fermenting bacterial cell. Whether such conditions create the potential for further chemical synthesis leading to prebiotic chemistry on the threshold of life is an open question. However, among all of the extraterrestrial solar system bodies accessible to direct exploration, Titan is the only one with a demonstrated organic inventory, and displays physical processes not unlike those here on Earth (Lorenz and Sotin, 2010).
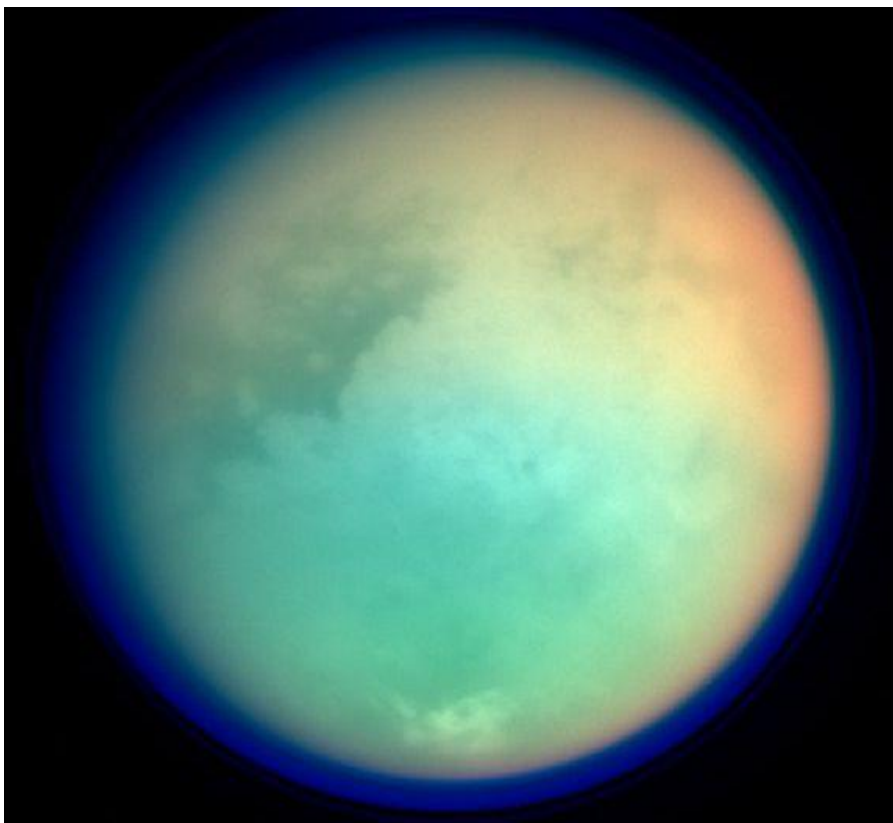

Figure 12. Titan's false color image reveals details of its surface and layers of haze in its atmosphere. Credit: Cassini Imaging Team, SSI, JPL, ESA, NASA.

Although at first glance Saturn's smoggy moon Titan and the planet Mars appear to have nothing in common but their color palette, the atmospheres of both worlds do contain an unlikely molecule: methane. Because ultraviolet sunlight easily breaks up methane, its detection implies a recent source. Hydrothermal vents, volcanic eruptions and even life are among the explanations scientists have offered. Primordial methane arising from the Titan surface decomposes in the upper atmosphere as a result of the action of solar ultraviolet radiation and charged particles. However, in

contrast to the giant planets, the low gravity of Titan is insufficient to retain the liberated hydrogen, which instead escapes to space. Recycling of the products of atmospheric photochemistry to regenerate methane is extremely limited and compounds rich in the number of carbon atoms (complex organic compounds) accumulate. As the chemistry continues to develop in the cold atmosphere, condensed organic aerosols nucleate and grow (Fig. 12). This condensed phase within the atmosphere provides a new setting for organic chemistry to proceed. The gas-phase organic species and organic aerosols collect on the surface, existing as liquid or solid phases according to their thermodynamic properties. Thus the coupled atmosphere/surface Titan system is an active laboratory for synthesis of complex organic compounds.

Recently, researchers investigating the interior structure of Titan now make the link between the model predictions (Tokano and Neubauer, 2005) and the observations (Lorenz et al., 2007) and conclude that an internal ocean of liquid water is present (Sotin, 2008). This finding is in agreement with previous models of Titan's evolution (Grasset, 1996; Tobie et al., 2006) that predicted an ammonia-rich deep ocean. If the presence of a liquid water ocean is confirmed, one of the conditions for organic molecules and perhaps life to form and develop is satisfied for another solar system body. Data from Titan could then help to elucidate the formation of organic material in an icy satellite, and to address the question of whether this ocean could be habitable. With its dunes, lakes, channels, mountains, and cryo-volcanic features, Titan is an active place that physically resembles Earth, with methane playing the role of water, while ice plays the role of silicate rock. The study of geological processes acting on these different materials by Cassini-Huygens and future missions will help us to understand other possible cycles of the elements and organic molecules that contrast, at least geochemically, with our own Earthly environment. The realization of Titan's potential for providing key insights into planetary organic chemistry, and possibly insights into chemistry leading to life has motivated the choice of a Titan Flagship mission for consideration for launch in the next decade. Whatever the outcome, there will be surprises in store.

Having whittled down the number of planets with the wherewithal to sustain life, we now turn to particular detection methods grounded in the theory of life's origin and early evolution outlined above.

6. HOW MIGHT WE FIND IT?

At bottom life hydrogenates carbon dioxide. But so does serpentinization—to methane—hence the problem of diagnosing its source (Mumma et al., 2009) (Table 2). However, this abiotic process does not appear to produce acetate or acetic acid (CH_3COOH) in measurable quantities—only the acetogenic bacteria do that. On the early Earth it seems that the homoacetogens were the first to resolve the tension between CO_2 and H_2 via the autotrophic acetyl coenzyme-A pathway (Fig. 7). The acetyl co-A pathway employs two separate tributaries; one Ni-Fe directed, merely reduces CO_2 to CO, while the other, initially molybdenum, or tungsten-directed, reduces CO_2 through to a methyl group. The CO and the -CH_3 are then assembled on the nickel-bearing acetyl coenzyme-A synthetase. Such a complex dual delivery system could not be prefigured by serpentinization but requires a chemiosmotic drive, as did the origin of life itself (Nitschke and Russell, 2009). Homoacetogens can compete successfully against the methanoarchaea for H_2 and CO_2 in the cold, as can the sulfate-reducing acetate-generating bacteria (Krumholz et al., 1999). Thus we argue that acetate or acetic acid effluent (depending on pH) from putative microbes on wet rocky planets would be a more reliable indicator of life than methane. It is the exhalation of acetate that points to an unequivocal biotic source because the serpentinizing process is generally too reducing to produce acetate in any quantity. For example, at Lost City only methane and ethane are recorded in the millimole range (Proskurowski et al., 2008; Konn et al., 2009). Moreover our hydrothermal vent experiments to date (Mielke et al., in prep) also indicate that no significant concentrations of <u>abiotic</u> acetate were produced in spite of the simplicity of the biological pathway (Fig. 7 and Table 2). However, these two processes would dominate in an anaerobic planet though—another caveat this—the ratio between acetate and methane produced from the Earth's deep biosphere may be only one part in five (Ljungdahl, 2009).

Nevertheless, as there is every reason to believe that the same chemical and electrochemical tensions would occur on other terraqueous worlds we suggest that the detection of acetate (in situ) or, where conditions are more acidic, acetic acid (remotely) become a primary focus. Admittedly, acetate (or acetic acid where pH is low enough) and its derivatives are much more difficult to detect than methane. Moreover, like other organic molecules, acetate is highly unstable in the face of hard UV and oxidants, so its photo-oxidized derivatives should also be considered (Yung et al., 2010).

Beyond our solar system, only those rocky silicate planets with a high enough oxidation state and gravity field to harbor ice, water and carbon dioxide are likely to support life, features that the Terrestrial Planet Finder missions will be able to determine (Kuchner and Seager, 2005; Charbonneau et al., 2009). And of course, if evolution had taken its course to include oxygenic photosynthesis as the ultimate in autotrophy, then

oxygen itself would be indicative of burgeoning life, at least in the presence of traces of reduced gases such as methane or hydrogen (Hitchcock and Lovelock, 1967) (Table 2). Even a world which had evolved to employ non-oxygenic photosynthesis might be expected to host gravity-defying structures such as stromatolites—a further *in situ* target for life detection (Russell et al., 1999; Westall, 2005; Allwood et al., 2009). But even in this case, were the structures made of calcite, they too would be prone to disintegration under the impact of hard UV (Stoker and Bullock, 1997).

What of the possibility of there being life on the newly discovered extrasolar water world, GJ 1214b (Charbonneau et al., 2009)? This planet is six and a half time the mass of the Earth and appears to have a hydrogen-helium envelop. Whether carbon dioxide, critical as a source of carbon and as an electron acceptor for life, is also featured is not known. However, as it orbits a star only 13 parsecs away it is amenable to further observation from our planet.

7. DISCUSSION AND CONCLUSIONS

A theory of how the biosphere emerged, based on our knowledge of this planet, is couched in the context of the expected differentiation of all relatively large terraqueous globes both in our own, and other comparable solar systems. While differentiation to the various spheres of the early Earth may be considered largely a response to radiogenic and gravitational heat production in the interior, an effect of these differentiations is to gather electrons in the core in native iron (Fe^0 with its full complement). However, early core formation still left the upper mantle relatively electron-rich (in Fe^{II}-bearing minerals), compared to the exhaling and accreting oxidized volatiles (H_2O, CO_2, NO) that composed the early volatisphere. The atoms comprising these oxidized molecules share electrons and are the potential electron acceptors for dissimilatory metabolism of the kind that led to the emergence of the biosphere.

Because CO_2 and NO could permeate into the ocean and because the ocean could percolate within the upper crust, there was a blurring of the redox states between the crust and the hydrosphere/atmosphere—a blurring that led to the emergence of the last and most complex sphere to differentiate—the biosphere. First the crust became somewhat oxidized through the process of serpentinization while a small portion of the H_2O, CO_2 and NO was reduced to H_2, $CH_4 > C_2H_6 >> C_3H_8 >> C_4H_{10}$ and NH_3. These volatiles were returned to the ocean and atmosphere. However, in the early stages of development of our planet their egress was inhibited by the co-precipitated Fe, Ni, Co, Mo and W sulfides or oxides, set in porous mounds comprised of carbonates and hydroxysilicates, precipitated where alkaline hydrothermal springs interfaced the acidulous ocean. These

inorganic outer margins of the mound steepened the redox gradient precipitously. Protons from the early ocean penetrated the outer boundaries of the mounds and pushed the electrochemical potential for formate production from CO_2 to well within the range accessible to the hydrothermal, electron-donating H_2.

The catalytic activities of the transition metals precipitated in the mound were vital to such syntheses. More complex intermediates such as carboxylic, amino, and eventually nucleic acids and their polymers, were generated in this milieu by these same chemiosmotic forces. This compartment-based autogenesis evolved to autotrophic life as electrons looked for a place to rest (in Szent-Györgyi's famous phrase). Heterotrophy—a digestive process using pre-existing biotic molecules—had to await autotrophy. Life involves eddies of electrons prior (in the long run) to their detrital dumping or egress into the volatisphere. Just as heat is radiated to cold space, so too electrons in geochemically, metabolically and photolytically produced H_2, are returned to the ether. The main early effluents from emergent life were methane and acetate. Acetate, being an overwhelmingly biotic product, would be a less ambiguous guide to microbial activity on other planets. However, because mere chemo-biosynthesis is a relatively inefficient mechanism for drawing down CO_2, effluents will be close to detection limits (Rosing, 2005).

Solar energy exploitation by bacteria on the other hand, greatly increases production of the surface biosphere. And oxygenic photosynthesis is even more effective, though the release of oxygen to the atmosphere had to await the oxidation of exposed reduced entities such as ferrous-iron- and manganous-bearing minerals and organic molecules. But the discovery of oxygen in an extraterrestrial water-world, particularly accompanied by traces of methane or hydrogen, would be an incontrovertible indication of life (Hitchcock and Lovelock, 1967). Equally, dry planets, whatever their interior makeup, lacking the universal solvent to mediate the resolution of geochemical disequilibria, will also be lifeless.

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