

## Geodynamic and metabolic cycles in the Hadean

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**Abstract.** High-degree melting of hot dry Hadean mantle at ocean ridges and plumes resulted in a crust about 30 km thick, overlain in places by extensive and thick mafic volcanic plateaus. Continental crust, by contrast, was relatively thin and mostly submarine. At constructive and destructive plate boundaries, and above the many mantle plumes, acidic hydrothermal springs at  $\sim 400^\circ\text{C}$  contributed Fe and other transition elements as well as P and  $\text{H}_2$  to the deep ocean made acidulous by dissolved  $\text{CO}_2$  and minor HCl derived from volcanoes. Away from ocean ridges, submarine hydrothermal fluids were cool ( $\leq 100^\circ\text{C}$ ), alkaline (pH  $\sim 10$ ), highly reduced and also  $\text{H}_2$ -rich. Reaction of solvents in this fluid with those in ocean water was catalyzed in a hydrothermal mound, a natural self-restoring flow reactor and fractionation column developed above the alkaline spring. The mound consisted of brucite, Mg-rich clays, ephemeral carbonates, Fe-Ni sulfide and green rust. Acetate and glycine were the main products, some of which were eluted to the ocean. The rest, along with other organic byproducts were retained and concentrated within Fe-Ni sulfide compartments. These compartments, comprising the natural hydrothermal reactor, consisted partly of greigite ( $\text{Fe}_5\text{NiS}_8$ ). It was from reactions between organic modules confined within these inorganic compartments that the first prokaryotic organism evolved. These acetogenic precursors to the bacteria diversified and migrated down the mound and into the ocean floor to inaugurate the “deep biosphere”. Once there they were protected from cataclysmic heating events caused by large meteoritic impacts. Geodynamic forces led to the eventual obduction of the deep biosphere into the photic zone where, initially protected by a thin veneer of sediment, the use of solar energy was mastered and photosynthesis emerged. The further evolution to oxygenic photosynthesis was effected as catalytic [Mn,Ca]-bearing molecules that otherwise would

have been interred in minerals such as ranciéite and hollandite in shallow marine manganeseiferous sediments, were sequestered and invaginated within the cyanobacterial precursor where, energized by light, they could oxidize water. Thus, a chemical sedimentary environment was required both for the emergence of chemosynthesis and of oxygenic photosynthesis, the two innovations that did most to change the nature of our planet.

### 1 Introduction

The Earth's internal thermal energy is mainly degraded through convection. Heat is transferred to the surface by a convecting mantle, to be discharged through volcanoes and hydrothermal springs into the ocean and atmosphere (the volatisphere). Chemical disequilibrium between reduced mantle and oxidized volatisphere is focused at springs and seepages on land or on the ocean floor. In turn this chemical energy is degraded through metabolism. Today metabolism relies on convection for supply of nutrients in the ocean, and on convection in the atmosphere for irrigation and chemical weathering of the land. The springs and seepages are oases of life in both realms.

At a broader scale and at slower rates, global geodynamic processes generate fresh, reduced rock surfaces that provide energy and supply nutrients to life. This coupling of metabolism to convection was directly implicated in the onset of life, which probably emerged at least 4 Gyr ago at moderate temperature seepages (Russell et al., 1988, 1994).

Reconstruction of the conditions that drove life to emerge and evolve its metabolic cycles is the main task of this paper. We begin by considering what present-day processes offer to the understanding of the conditions on the surface and in the interior of the Hadean/Archaean Earth, then suggest a scenario for the onset of life and its colonization of the ocean floor. This journey from geodynamics, through

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**Table 1.** Examples of high- and moderate-temperature submarine springs.

Parameter	J da Fuca <sup>1</sup>	Rainbow <sup>2</sup>	Lost City <sup>3</sup>	Eyjafjördur <sup>4</sup>
T°C	224°	365°	40°–75°	71.4°
pH	3.2	2.8	≤9.8	10.03 (24°C)
duration yr	>1000	>1000	>30 000	11 000
H <sub>2</sub> mmol	na	13	0.43	na
H <sub>2</sub> S	3.5	1.0	0.064	0.01
SO <sub>4</sub>	0	(0)	5.9–12.9	0.2
Fe	18.74	24	na	0.00014
Mn	3.58	2.25	na	0.0000018
Mg	0	0	9–19	0.01
Ca	96.4	67	22	0.061
Na	796	553	482	3.4
K	51.6	20	na	4.2
SiO <sub>2</sub>	23.3	6.9	na	1.6
CO <sub>2</sub>	≤4.46	na	na	0.57
Cl	1087	380	548	1.26
Co	na	0.013	na	na
Ni	na	0.003	na	na
Zn	0.9	0.16	na	na
Mo	na	0.000002	na	na

Data for column <sup>1</sup>. Von Damm (1990), <sup>2</sup>. Douville et al. (2002), <sup>3</sup>. Kelley et al. (2001) and Früh-Green et al. (2003), <sup>4</sup>. Marteinson et al. (2001). Temperatures at the base of the convection cells developed at oceanic spreading centres and the off-ridge systems are presumed to be ~400°C and ~115°C, respectively (Bischoff and Rosenbauer, 1984; Wenner and Taylor, 1971). The pH of the pristine alkaline fluid is also likely to have been ~11 (Neal and Stanger, 1983, 1984). The estimates of the duration of high-temperature discharge is taken from Elderfield and Schultz (1996). “na” signifies not analysed.

geochemistry to biochemistry leads us to conclude that obduction of oceanic crust facilitated the evolutionary jump to photosynthesis.

## 2 The modern oceanic crust

### 2.1 Birth and death of oceanic crust

A complete plate tectonic cycle starts with the formation of crust at a ridge and ends with its recycling to the mantle at a subduction zone. Continental crust forms above a subduction zone, a result of the melting of subducting oceanic crust and/or its dehydration, which triggers partial melting in the overlying mantle and the development of hydrous magmas. Superimposed on the plate tectonic cycle is the formation of oceanic islands and oceanic plateaus, which are generated by partial melting in mantle plumes.

### 2.2 Modern hydrothermal systems – how they work

Five main types of hydrothermal fluids circulate through modern oceanic crust: three high temperature types (≤400°C) operate at oceanic ridges, above plumes and in back-arc basins respectively; an intermediate type occurs on ridge flanks (≤115°C); and the last, far cooler, on the deep

ocean floor (Anderson et al., 1977; Bonatti et al., 1983; Von Damm, 1990, Cathles, 1990; Sedwick et al., 1994; Kelley et al., 2001; Wheat et al., 2002; Früh-Green et al., 2003) (Table 1).

The temperature of the very hot springs, driven by magmatic intrusion, is controlled largely by the two-phase boundary of water and its critical point (Bischoff and Rosenbauer, 1984). Temperatures in modern hydrothermal convective systems, which bottom at an overall water column depth of 4 km or so, tend to peak at ~400°C. The fluids in the downdrafts become acidic (pH ~3) through the release of protons while Mg<sup>2+</sup> is fixed in serpentine and brucite (Janecky and Seyfried, 1983; Douville et al., 2002). These acidic solutions dissolve, transport and exhale the transition metals, some phosphate, H<sub>2</sub>S and H<sub>2</sub>, at black smokers (Table 1) (Von Damm, 1990; Kakegawa et al., 2002).

The temperatures and compositions of intermediate-temperature hydrothermal convection cells are controlled by exothermic reactions and the rheology of the newly serpentinized mafic-to-ultramafic wall rock of the conduits. So far the fluid from only one entirely submarine example of ultramafic interaction has been sampled, the “Lost City” field, 15 km from the Mid Atlantic Ridge (Kelley et al., 2001; Früh-Green et al., 2003). The pH of this water approaches

10 as  $\text{Ca}(\text{OH})_2$ ,  $\text{HCO}_3^-$  and  $\text{H}_2$  are eluted, and the temperature is 70° to 75°C (Table 1) (Kelley et al., 2001). Another broadly comparable system has been discovered in a fjord off the north coast of Iceland (Marteinsson et al., 2001; Geptner et al., 2002). Porous cones of Mg-rich clay (saponite), some tens of metres high, characterize this warm (72°C) alkaline (pH 10), though fresh-water submarine spring (Table 1).

Still farther from ridges, even cooler circulation is driven by heat within the uppermost crust. Small closed convection cells are evenly spaced with a periodicity of about 7 km, with thermal cusps around 20°C (Anderson et al., 1977).

### 3 Hadean/Archaean ocean/atmosphere, oceanic crust and global dynamics

#### 3.1 The volatilisphere

According to oxygen isotope analysis of the oldest known zircons, an ocean is assumed to have condensed on Earth by 4.4 Ga (Wilde et al., 2001). The atmosphere contained  $\text{CO}_2$  and  $\text{N}_2$ , some HCl,  $\text{SO}_2$ ,  $\text{S}^0$  and minor amounts of  $\text{H}_2$  and Ar (Kasting, 1993; Kasting and Brown, 1998; Pavlov and Kasting, 2002). Volcanogenic  $\text{CO}_2$  and HCl, augmented by output from high temperature acid springs, rendered the early ocean acidulous (pH 5–6) (Maisonneuve, 1982; Sedwick et al., 1994; Kasting, 1993; Macleod et al., 1994). The proportion of the  $\text{CO}_2$  depended on the balance between inputs from volcanic emissions and redissolution in the deep ocean and outputs via carbonation of the crust and of the dust thrown up by meteorite impacts (Alt and Teagle, 1999; Nisbet and Sleep, 2001). Transition metals and phosphate contributed by very hot springs remained in solution in this acidulous ocean (Kakegawa et al., 2002). Particularly important is  $\text{Fe}^{2+}$ , some of which was photo-oxidized to insoluble flocs of  $\text{FeOOH}$  at the ocean's surface (Braterman et al., 1983; Gaffey, 1997; Russell and Hall, 2002).

#### 3.2 Crustal structure and composition

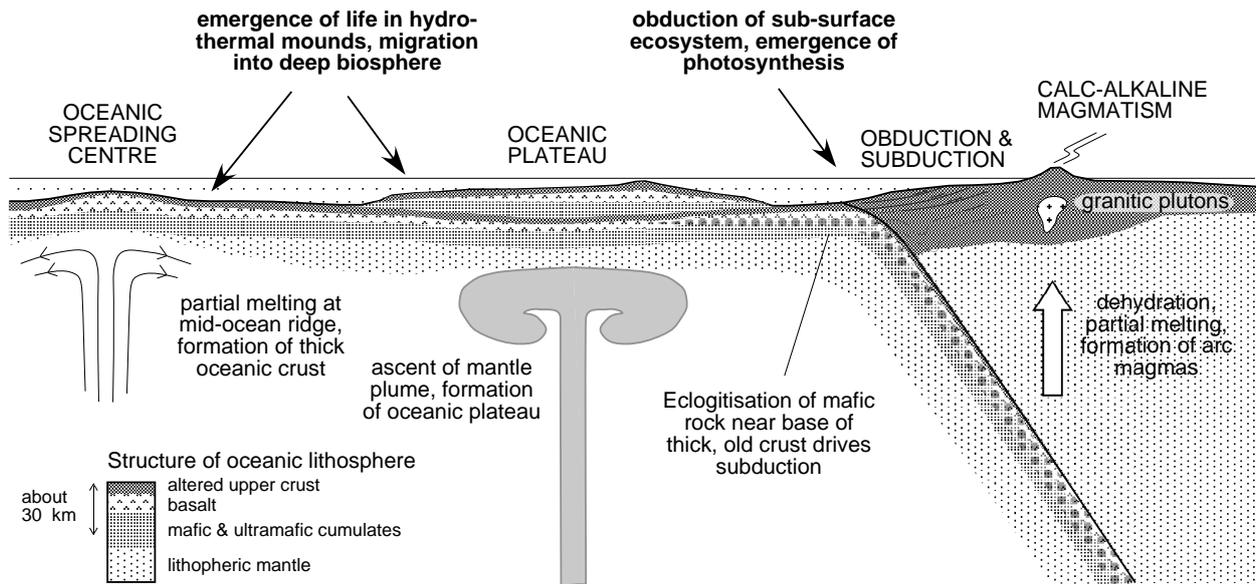
Heat production in the Hadean was at least 5 times that of the present day and it is probable that the mantle was several hundred degrees hotter than it is today (Turcotte, 1980). Because the dehydration reactions that control the amount of water recycled to the mantle are temperature dependent, the Hadean mantle was drier than its modern counterpart. The ocean contained most of the Earth's water and its volume may have been up to twice that of today's oceans (Bounama et al., 2001). Upwelling of hot, dry mantle at oceanic spreading centres generated an early Archaean crust about 30 km thick (Sleep and Windley, 1982; Arndt and Chauvel, 1990) (Fig. 1). Oceanic plateaus, even more extensive than Ontong Java, covered large parts of the oceanic crust with an additional 30 km of mafic and ultramafic igneous rock. Both the oceanic crust and plateaus were internally differentiated. In each an upper ~5 km-thick layer of magnesian basalt overlay

~10 km of gabbros and troctolites and 10 km or more of ultramafic cumulates (Francis et al., 1999; Foley et al., 2003).

The volume of continental crust in the early Archaean was a subject of intense debate in the 1980's. Geochemists tended to the interpretation that continental crust started to appear only around 3.8 Ga, the age of the oldest rocks known at that time. Since then several important discoveries have been made. The pre 4.2 Ga zircons provide evidence for the existence of granitic rocks in the Hadean (Froude et al., 1983; Compston and Pidgeon, 1986) and their oxygen isotopic compositions suggest that an ocean had condensed on Earth by 4.4 Ga (Wilde et al., 2001; Mojzsis et al., 2001). Direct or indirect evidence for very old continental crust is becoming more abundant: the 4 Ga Acasta gneisses (Bowring and Williams, 1999) contain 4.2 Ga zircons (Iizuka et al., 2002), and the recently discovered 3.8 Ga Porpoise Cove supracrustal rocks on the east coast of Hudson Bay have Nd isotopic compositions indicating assimilation of still older granitoids (Stevenson et al., 2003). Although such an early age for the onset of subduction and the generation of granites is not without its critics (e.g. Glikson, 1972; Whitehouse and Kamber, 2002), ultra-high-pressure metamorphic rocks do indicate that portions of the continental crust are routinely cycled deep into the mantle. These discoveries provide mounting support for Armstrong's (1981, 1991) model of rapid early continental growth. In this model, granitic continental crust was abundant by the end of the Hadean.

The topography of the Hadean planet differed radically from that of the modern Earth. Because Hadean granitic crust contained higher concentrations of radioactive elements it was hotter, less viscous, and thinner than modern continental crust (Sandiford and McLaren, 2002). And because the mantle also was hotter, the continental lithosphere was thinner. Oceanic crust, in contrast, was much thicker than modern oceanic crust, as thick or thicker than the early Archaean continental crust. The oceans were more voluminous and they flooded a greater portion of the Earth's surface. Most of the continents were submerged and only mountain ranges at convergent margins and vast volcanic plateaus occasionally breached the ocean surface (Arndt, 1999) (Fig. 1). Thus there was little subaerial weathering and erosion of the mainly submerged continental masses and comparatively little clastic sedimentation.

Hydrated oceanic crust was continually cycled back into the mantle. At the base of the thickest sections, where oceanic plateaus had erupted onto the oceanic crust, pressures were sufficient to convert plagioclase to garnet. The downward drag of these dense eclogitised segments and the underlying dense Fe-rich ultramafic cumulates initiated subduction. Once started, the entire basaltic and gabbroic portion of the crust converted to eclogite, and plunged into the mantle (cf. Holmes, 1931). The earliest subduction zones probably were steeply dipping, rather than shallow, as is commonly assumed (Fig. 1) (Karsten et al., 1996). The upper layers of the crust dehydrated and triggered the melting in the



**Fig. 1.** Cross-section illustrating mantle convection on the Earth at the Hadean/Archaean boundary (Campbell et al., 1989; Davies, 1992; Foley et al., 2003; Fitton et al., 2004). Life is held to have emerged at an alkaline seepage site. An early batch of prokaryotic colonies was conveyed toward a plate margin where it was obducted into the photic zone, facilitating the onset of photosynthesis (Fig. 2). (At times and in places plume-type convective mass transfer may have involved the whole mantle).

over-riding mantle that gave rise to the magmas parental to continental crust. The uppermost parts of the oceanic crust obducted to form accretionary prisms of the type discussed by Maruyama (1997) and Foley et al. (2003). These prisms obliterated any nascent oceanic trenches, a process that was highly significant, as we shall see, to the development of photosynthesis.

### 3.3 Hydrothermal circulation

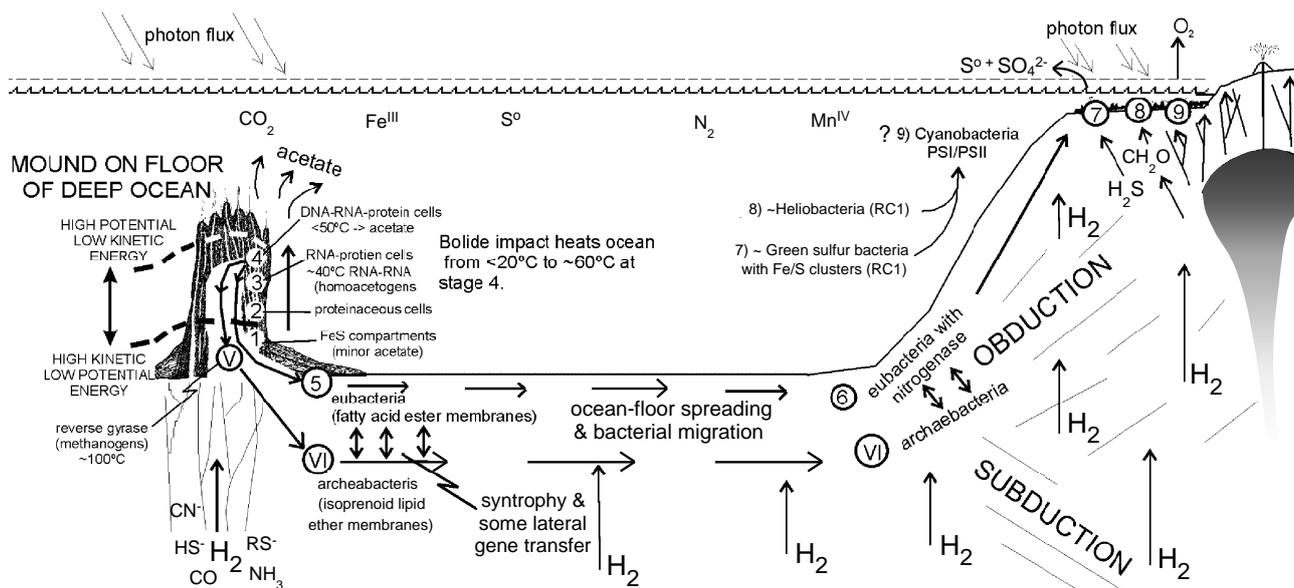
If we assume that the 400°C springs developed at constructive plate margins were comparable to those emanating from the ultramafic crust at the Rainbow field, the highly reduced acidic fluids would have carried about 20 mM of  $\text{Fe}^{2+}$  to the ocean (Von Damm, 2000; Douville et al., 2002; Allen and Seyfried, 2003) (Table 1). With negligible marine sulfate in the Hadean (Farquar et al., 2000) there were no spontaneously precipitated protective anhydrite chimneys, and no black smokers. Hydrogen sulfide, reacting first with zinc, produced soluble but stable  $\text{ZnS}$  clusters as the solutions cooled on exhalation (Luther et al., 1999). Given the high remaining metal to sulfide ratio (Walker and Brimblecombe, 1985), much of the Fe and minor Ni stayed in solution in the acidulous ocean, though photo-oxidation of a proportion of the  $\text{Fe}^{2+}$  generated flocs of  $\text{FeOOH}$  (Braterman et al., 1983).

In marked contrast, the off-ridge springs would have had a similar temperature and chemistry to those of the present day ( $\leq 100^\circ\text{C}$  and pH 9–11, Table 1) (Shock, 1992; Macleod et al., 1994; Kelley et al., 2001; Russell and Hall, 2002; Foley et al., 2003). Similar solutions may have exhaled from faulted zones within the oceanic plateaus. Such alkaline so-

lutions could have provided  $\sim 10\text{mM}$  of  $\text{HS}^-$  to the seepage site (Macleod et al., 1994; Rahman, 2003). A mound of precipitates formed where these seepage waters met the acidulous ocean. The main precipitates were of brucite, iron and ephemeral calcium and magnesium carbonates, with subsidiary ferrous and ferric oxyhydroxides and iron > nickel sulfides (Russell et al., 1988, 1998).

### 3.4 Ocean temperatures

The temperature of the Hadean ocean is uncertain. The effective radiative temperature of the Sun then was about 70% of its present output (Sagan and Mullen, 1972; Bahcall et al., 2001). Only the presence of atmospheric greenhouse gasses,  $\text{CO}_2$  or  $\text{CH}_4$ , prevented the Earth from completely freezing over (Kasting, 1993). Indeed, temperatures may, on occasion, have approached  $100^\circ\text{C}$ . But, as mentioned above, there were several effective sinks for  $\text{CO}_2$  including the extensive volcanic plateaus and the dust raised by meteorite impacts (Nisbet and Sleep, 2001). These impacts on the other hand may also have vaporized the ocean from time to time, though temperatures were never so high that a Venus-like atmosphere persisted, where  $\text{H}_2$  loss depleted the hydrosphere. Very likely there were frequent oscillations from hot (impact and green-house induced), to cold and partially frozen, a consequence of solar radiation masking by local or galactic dust clouds (Maher and Stevenson, 1988; Kasting, 1993; Kasting and Brown, 1998; Alt and Teagle, 1999; Nisbet and Sleep, 2001). Very cold conditions were short-lived because of continuous and widespread volcanicity and exhalations of  $\text{CO}_2$ . Without the dampening capacity of large landmasses, con-



**Fig. 2.** Chemosynthetic life emerges at a warm alkaline seepage, differentiates into the precursors of the bacteria and archaea, and expands into the surrounding sediments and crust (Martin and Russell, 2003; Russell and Martin, 2004). From here a proportion is conveyed by ocean floor spreading toward a constructive margin produced partly by obduction. Once at the margin some of the cells happen to invade manganiferous sediments in the photic zone where, at a sulfurous spring, some evolve to exploit solar photons. Numbers 1–3 relate to life’s emergence, 4 marks the point of differentiation of the archaea from the bacteria. Roman numerals V–VII mark evolutionary stages of the archaea, and 5 and 6 show stages of evolution of the bacteria in the deep biosphere. Photon energy may have been first mastered by the green sulfur bacteria (7), followed by the heliobacteria (8) (Vermaas, 1994; Baymann et al., 2001). These photosynthesizing bacteria had probable appeared by the early Archaeans (Westall et al., 2001). Oxygenic photosynthesis (9) is a further evolutionary development, though the age of its emergence is highly controversial and its presence in this diagram is speculative (not to scale).

ditions at the ocean surface were likely to have been storm-ravaged whatever the temperature – too tempestuous for the collection of lipids and the focusing of energy and materials to convert them to cells with enzymes, metabolites and genomes.

Notwithstanding an earlier suggestion for a thermophilic start to life (Russell and Hall, 1997), because of the fragility of RNA, and because the acetogenic pathway operates best below about 50°C, we recognise that life is unlikely to have emerged at temperatures much above 40°C (Forterre, 1996; Schink, 1997; Moulton et al., 2000; Brochier and Philippe, 2002). And because a thermal gradient is required to drive convection, we suggest that life’s emergence had to await a period, or “window of opportunity” when oceanic temperatures were low, perhaps around 20°C (but see Schwartzman and Lineweaver, 2004, for a contrary view). However, once life had emerged it had to survive the Hadean periods of high temperature. How this was done will have to be addressed in our hypothesis of life’s emergence and early evolution.

## 4 Chemical contribution to the onset of life

### 4.1 The hydrothermal mound

Haeckel (1892, p. 414) considered life to have emerged from an “inorganic formative fluid”, and Leduc (1911, p. xv) sug-

gested that “the chain of life is ... a continuous one, from the mineral at one end to the most complicated organism at the other”. In Leduc’s view the first compartments to store the potential energy that drove life to emerge were also inorganic. These prescient ideas were ignored, partly because they seemed to hark back to theories of spontaneous generation put paid to famously by Pasteur, and partly because scientists were loath to consider anything but an organic origin for any organic being. The organic view has held sway for 75 years (Bada, 2004). However, the inorganic hypothesis has since been disinterred and we suggest that a stable, long-lived alkaline submarine seepage of moderate temperature satisfies Haeckel’s expectations (Russell et al., 1988, 2003). Further, we suggest that Leduc’s inorganic compartments may have comprised catalytic iron(nickel) sulfides generated at this same seepage (Russell et al., 1994). This idea is given further significance by the recognition that iron and sulfur comprise the active centres to a protein with the longest pedigree, the electron transfer agent known as ferredoxin – a metabolic enzyme which is strongly electronegative with a potential close to that of molecular hydrogen (Eck and Dayhoff, 1966; Hall et al., 1971).

Portions of a hydrothermal mound comprising freshly precipitated films of iron sulfide in the form of disordered nanometric mackinawite ( $\text{Fe}_{1+x}\text{S}$ ) and minor greigite ( $\text{Fe}_5\text{NiS}_8$ ) offered semipermeable and semiconducting containers for

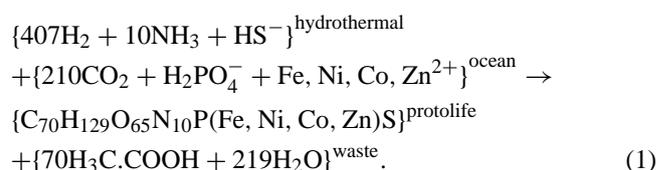
both organic synthesis and retainment (Russell and Hall, 1997; Filtner et al., 2003; Wolthers et al., 2003). Strong gradients developed at the outer margins of such a mound where the reduced alkaline hydrothermal solution interfaced the cooler, more oxidized Hadean ocean. Potentials focused across the iron sulfide membranes were hydrodynamic (between buoyant hydrothermal solution and ocean), thermal (<20° to 115°C), chemical (between hydrothermal H<sub>2</sub> and CO<sub>2</sub>) and electrochemical (between redox couples H<sup>+</sup>/H<sub>2</sub> and Fe<sup>3+</sup>/Fe<sup>2+</sup>) (Russell and Martin, 2004). Electrons could also be gained from H<sub>2</sub>S and HS<sup>-</sup>.

Reduction of CO<sub>2</sub> or HCO<sub>3</sub><sup>-</sup> to CO with activated H<sub>2</sub> (as H·) is assumed to take place on nanocrystals of mackinawite and greigite (Russell et al., 1998; Russell and Martin, 2004). Further reduction to methane thiol (CH<sub>3</sub>S<sup>-</sup>), involving H· is activated hydrogen, i.e. a highly reactive hydrogen atom and HS<sup>-</sup>, is strongly thermodynamically favoured (Schulte and Rogers, 2004). Heinen and Lauwers (1996) have produced methane thiol directly by reduction of CO<sub>2</sub> with the concomitant oxidation of FeS to pyrite by H<sub>2</sub>S, as might be expected of the “pyrite-pulled” hypothesis of Wächtershäuser (1988). Huber and Wächtershäuser (1997) have reacted CO and CH<sub>3</sub>SH to produce acetate (H<sub>3</sub>C.COO<sup>-</sup>) in yields of 40% with respect to the thiol. Experimental conditions were 100°C at a pH of 6.4. These chemical and physical states can be met near the surface of the hydrothermal mound. It appears then that the first result of a reaction between an alkaline hydrothermal fluid and carbonic ocean water will be acetate. Indeed, acetate is the product of what is known as the acetyl coenzyme-A pathway – the most ancient of the metabolic pathways (Peretó et al., 1999; Russell and Martin, 2004).

In their experiments Huber and Wächtershäuser (1997) used a slurry of iron sulfide and nickel sulfide. However, Russell et al. (1998) pointed out that greigite and violarite (Fe<sub>2</sub>Ni<sub>4</sub>S<sub>8</sub>) are more likely to have been the catalysts. The high acetate yields are an expression of the thermodynamic calculations of Shock et al. (1998), who demonstrated the reaction between CO<sub>2</sub> and H<sub>2</sub> with the production of acetate to be extremely favourable (exergonic). The structure of greigite (Fe<sub>5</sub>NiS<sub>8</sub>) is strikingly similar to the active centres (e.g. Fe<sub>4</sub>NiS<sub>5</sub>) of the enzymes presently involved in the reduction of CO<sub>2</sub> and the formation of acetate (Vaughan and Craig, 1978; Russell et al., 1994, 1998; Russell and Martin, 2004). These enzymes are known as carbon monoxide dehydrogenase/acetyl co-enzyme-A synthase (CODH/ACS) (Dobbeck et al., 2001; Drennan et al., 2001; Darnault et al., 2003). The same enzymes are known to have the facility to activate H<sub>2</sub> (Menon and Ragsdale, 2000).

We can say then that the first microbe used the energy and materials within the hydrothermal solution and the ocean to generate acetate and water as waste products, i.e. it was an “acetogen” (Russell and Martin, 2004). The emergence of life and the generation of acetate waste within the natural hydrothermal reactor can be considered rather as we might

characterize mineral precipitation at a hot spring, though as soon as organic molecules are formed in the process they have the effect of inhibiting mineral growth (e.g. Rickard et al., 2001). Indeed, we can think of the active centres of the metalloproteins as “still-born” mineral clusters. The approximate and highly simplified formula for “proto-life” used here [C<sub>70</sub>H<sub>129</sub>O<sub>65</sub>N<sub>10</sub>P(Fe,Ni,Co,Zn,Mo)S] is gleaned from a number of sources (Redfield et al., 1963; Orr, 1978; Morel and Hudson, 1985; Faggerbakke et al., 1996; Macalady and Banfield, 2003). The trace metal contents are rather exaggerated in keeping with their likely contribution to the first living cells. The reactions that generated this proto-life and waste can be put notionally as:



Note the high waste-to-protolife molecular ratio.

In this explanation the hydrothermal mound is viewed as a self-restoring catalytic flow reactor that synthesized acetate (Russell and Martin, 2004). More complex organic molecules were minor by-products of the reaction, by-products that were to optimize acetate production. Of particular significance was the amino acetic acid glycine (<sup>+</sup>H<sub>3</sub>N.CH<sub>2</sub>.COO<sup>-</sup>), produced in hydrothermal experiments by Hennet et al. (1992). Once glycine appeared in the sulfide compartments, the redox and pH gradients came into effect (Russell and Hall, 1997, 2002). The alkaline mounds constituted the hydrogen electrode, or cathode, and the photolytic ferric iron flocculants (denoted by Fe<sup>III</sup>) aggregated at the mound’s exterior, acted as a positive electrode. The Fe<sup>III</sup>/Fe<sup>3+</sup> provides a fraction of the potential, augmented by the exterior protons, that results in polymerization (Russell and Hall, 1997, 2002). Fe<sup>III</sup> accepted the electrons ultimately contributed by hydrothermal H<sub>2</sub>. Most prokaryotes near the root of the evolutionary tree can use Fe<sup>III</sup> as an electron acceptor, supporting the notion that it was the first to fulfill this vital role (McFadden and Shively, 1991; Liu et al., 1997; Pace, 1997; Russell and Hall, 1997; Vargas et al., 1998; Reysenbach and Lovley, 2002).

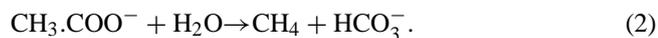
Today we recognize the power of light to directly drive much metabolism. In the Hadean the photolytic Fe<sup>III</sup> represented a “borrowed light” that energized and helped drive life’s emergence (Cairns-Smith et al., 1992; Russell and Hall, 2002). In theory, the electrochemical potential approaches one volt (Russell and Hall, 1997; Russell et al., 1998); in practice, Russell and Hall (2002) and Filtner et al. (2003) have demonstrated that an FeS membrane, spontaneously precipitated at the interface between solutions containing 10 mM of Fe<sup>2+</sup> on the one side, and 10 mM HS<sup>-</sup> on the other, can hold a tension of 600 to 700 mV for several hours. The gradients have the potential to drive the polymerization of inorganic phosphate if water activity

were low (Baltscheffsky, 1996). Polymerization may have taken place on the surfaces of closely packed mackinawite or greigite nanoclusters making up the inorganic membrane (cf. Huber and Wächtershäuser, 1998, 2003; de Zwart et al., 2004). In turn, and on the same surfaces, the pyrophosphate might have polymerized the glycine to form homopeptides. Alternatively, local generation of CO or COS upon sulfide could have driven polymerization (Huber and Wächtershäuser, 1998; Huber et al., 2003; Leman et al., 2004).

Once primitive peptides formed they will have coordinated the building blocks of greigite (e.g.  $[\text{Fe}_2\text{S}_2]^+$ ,  $[\text{Fe}_4\text{S}_4]^{2+}$  and perhaps  $[\text{Fe}_4\text{S}_6\text{Ni}]^+$ ) that had been inhibited from further growth by organic sulfides such as ethane thiol ( $\text{CH}_3\text{CH}_2\text{S}^-$ ) (Bonomi et al., 1985; Stevens and Kurtz, 1985). This was the beginning of the organic take-over from a mineral based prebiotic chemistry (Milner-White and Russell, 2005). These peptides may have contributed to a mixed polymer membrane, more stable and flexible than its inorganic precursor, yet with sequestered sulfides and phosphate, still able to gain electrochemical energy and nutrients from outside the individual cells (cf. Cole et al., 1994).

#### 4.2 Evolution in the mound

Newly evolved acetogens were the forerunners of the bacteria. However, evolution in the mound extended beyond mere optimization of the chemotrophic acetate reaction (Martin and Russell, 2003). The next step was the adaptation to organotrophy, the digestion of the reduced carbon and energy to be found in dead cells. A minority of cells, derived from those that emerged at around 40°C, exploited the potential offered at higher temperature elsewhere in the mound where the kinetic energy was greater and the activation energy required for reduction, through acetate, all the way to methane, was lower. That the first “methanogens” may have evolved while still in the mound, is argued because there is even more energy to be had in the full reduction of  $\text{CO}_2$  (Amend and Shock, 2001). Moreover, the metalloenzymatic machinery required for acetogenesis and methanogenesis is similar, though the structures of the organic carbon/nitrogen catalysts are rather different (Fontecilla-Camps and Ragsdale, 1999; Thauer, 1998). Moreover, methanogenic archaea can derive energy by generating methane from the acetate waste from neighbouring acetogens (Madigan et al., 2000):



Russell and Hall (2002) suggested that such methanogenic cells were the precursors of the archaea, the sturdy but slowly evolving second domain of the prokaryotes (Woese et al., 1990). If so, the last common ancestor of life occupied the very hatchery in which life first emerged, and the most significant of all cellular differentiations, that between the bacteria and the archaea, probably took place before the mound was evacuated (Koga et al., 1998; Martin and Russell, 2003). Up

till this time of divergence, genes were shared like software packages in what may be called a cellular cooperative. Eventually there was a differentiation of cells as opportunities for exploratory evolution and specialization in this previously empty habitat presented themselves, a differentiation partly driven by entropy – random changes in genes that eventually gave mutually exclusive phenotypes (Wicken, 1987). By this stage  $\text{Mn}^{\text{IV}}$  and  $\text{S}^0$  had joined  $\text{Fe}^{\text{III}}$  and  $\text{CO}_2$  as electron sinks.

In summary we can say that bacteria were initially suited to low to moderate temperatures, and the archaea originally evolved from them to withstand relatively high temperatures (i.e. ~55°C). But the propensity to live well above 40°C was passed back to the nascent bacteria through genetic transfer. A period of high ambient temperature, caused either by an impacting large meteorite or a  $\text{CO}_2$  greenhouse (Kasting and Akerman, 1986; Kasting and Brown, 1998; Nisbet and Sleep, 2001) could explain why the last common ancestor of all life may have been a thermophile, perhaps living at 50° to 60°C (Gaucher et al., 2003). Whatever the heating event, it was from the surviving community that the evolutionary tree was seeded.

Representatives of, and in, both domains found it advantageous to live syntrophically. Cells would have relied upon their neighbours to swap genes, provide some of the nutrients and to remove some of the waste (e.g. Eq. 2) (Morita, 2000). Unfortunates that were entrained within the hydrothermal solution and dispersed to the ocean could not have survived such dilution of nutrient or ocean-evaporating impact events (Sleep et al., 1989; Bjerrum and Canfield, 2002). The only way out was down – down onto the ocean floor and into the warm chemical sediments and permeable basalts below.

#### 4.3 Inauguration of the deep biosphere

Growth and expansion of the colonies of acetogens and methanogens followed the redox front laterally out of the mound and into the surrounding sediments. Colonization of the entire seafloor and upper crust was relatively rapid as microbial colonies were entrained in aqueous advection currents.  $\text{H}_2$  continued to be the available fuel, diffusing into the sediments and volcanic rocks from hydrating crust and mantle (Apps and van der Kamp, 1993).  $\text{H}_2$  was also provided by some of the fellow metabolizing cells within the syntrophic communities (Wolin, 1982; Towe, 1996).  $\text{CO}_2$  for biosynthesis continued to be available in downward percolating ocean water. And photolytic  $\text{Fe}^{\text{III}}$ , already deposited on the ocean floor, would have continued to act as a terminal electron acceptor so that electrochemical potential was maintained. At some stage fatty acids and lipids would have started to space out and replace much of the protein in the membrane (Martin and Russell, 2003).

Once life had emerged and gained a foothold in the sediments and hydrated volcanics of the ocean bottom it would have been extremely hard to eradicate. Strong Earth

tides resulting from the shorter day and lunar cycle and the closer moon continuously pumped the required nutrients from above and below through fractures in the upper crust (Davis and Becker, 1999). Only Fe<sup>III</sup>, the main electron acceptor in the chemical sediments, may have been in short supply. Even so, a small flux of H<sub>2</sub> was enough to prevent the decay of cellular material and the racemization of peptides (Morita, 2000).

Thus the deep biosphere was born (Parkes et al., 1990, 1994; Pedersen, 1993; Thorseth et al., 1995; Wellsbury et al., 1997; Whitman et al., 1998; Kotelnikova and Pedersen, 1997; Furnes et al., 2004). At this depth, as the thermal conductivity of saturated sediment and basalt is so low, the prokaryotes were well protected by a layer of insulating sediment and basalt from the thermal effects of impacts, even of those that may have caused the entire ocean to volatilize (Sleep et al., 1989).

## 5 Obduction and the emergence of photosynthesis

Given that conditions for life in the open sea were most inhospitable, how do we explain the emergence of photosynthetic organisms in the full glare of hard UV from the young sun (Canuto et al., 1982)? We suggest that obduction brought microbial consortia from the deep ocean floor into the photic zone. Because of the particular geometry of Hadean oceanic crust, chemical sediment overlying hydrated basaltic crust was obducted over the subducting, delaminated, eclogitised lower parts of the slab. Obduction of oceanic sediments, particularly of hydrated iron and manganese oxyhydroxides precipitated on the margins of volcanic chains, and of the hydrated basalt beneath, passively transported some bacterial colonies into shallow water and into the photic zone. Cells were protected from deleterious solar radiation beneath a mineral coating, perhaps within a biofilm (Cockell and Knowland, 1999). Opportunistic protection by superposed minerals and mineral excretions are well-known prokaryotic protective gambits (Phoenix et al., 2001). And the absorption and accumulation of manganese is also likely to have conferred resistance to radiation (Daly et al., 2004). In these conditions some bacteria near the surface further augmented their resistance to solar radiation by developing a UV pigment protector from a ring of organic bases. Pigments comprising macrocyclic aromatic rings probably date back to at least 4 Ga (Pratt, 1993). Single ions of Fe, Mg, Co, Ni, Cu and Zn can be sequestered individually in variants of what is known as the corrin or tetrapyrrole ring, itself comprising four C/N rings (Pratt, 1993; Eschenmoser, 1998; Allen, 2005). Pigments developed for photoprotection could then have been adapted as electron transfer agents, as photosynthetic reaction centres and antenna proteins (Mulikidjanian et al., 1997; Allen, 2005).

### 5.1 The first photosynthesists

The process of photosynthesis was mastered at least by the early Archaeon (Westall et al., 2001). The first photosynthesizing bacterium may have been a precursor to the green sulfur bacteria (Baymann et al., 2001). Like some pre-photosynthetic bacteria, these bacteria relied lithotrophically on H<sub>2</sub>S as an electron donor. Just as in modern island arcs and accretionary prisms, hydrothermal H<sub>2</sub>S of magmatic or metasomatic derivation would have circulated through the sediments in the obducted pile (Fig. 2). In these conditions, a photosynthetic reaction centre (RC1) could have developed that catalysed the generation of elemental sulfur and water as waste, and gained electrons and protons in the process (Eq. 3).

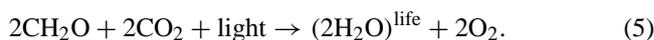
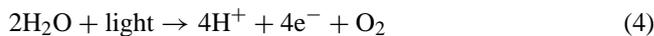


As we might expect of gradualistic evolution, the green sulfur bacteria continued to rely on iron sulfide clusters as electron transfer agents (Blankenship, 2002).

An evolutionary variant – a photosynthetic precursor of the heliobacteria bacteria – was able to fix CO<sub>2</sub> with electrons supplied indirectly by organic detritus (Vermaas, 1994). This change of electron source echoes the early evolution of biosynthesis, beginning with lithotrophs, followed by rapid and opportunistic adaptation to organotrophy (Sect. 4.2). The heliobacteria substituted a pigment as an electron transfer agent in place of some of the iron-sulfur centres (Allen, 2005). But they retained the use of photosynthetic reaction centre 1 (RC1) (Dismukes et al., 2001; Blankenship, 2002).

### 5.2 Oxygenic photosynthesis

The photosystem (PS2) employed by all cyanobacteria and plants to oxidize water only required gene duplication and gene splitting to descend from RC2 (Baymann et al., 2001). These genes could have been gained from green sulfur bacteria and/or heliobacteria (Michel and Deisenhofer, 1988; Baymann et al., 2001). In a variant of the hypothesis, Allen (2005) has argued that photosystem 1 (PS1) and PS2 diverged from reaction centres within a common anaerobic ancestor, perhaps a green filamentous bacterium. PS2 works in conjunction with PS1, itself also probably evolved from the first reaction centre (RC1) (Baymann et al., 2001). PS2 is capable of oxidizing two molecules of H<sub>2</sub>O (cf. the one molecule of H<sub>2</sub>S in the green sulfur bacteria shown in Eq. 3) during the generation of a single molecule of O<sub>2</sub>, gaining incrementally in the process four electrons and four protons for the fixation of carbon from CO<sub>2</sub> or HCO<sub>3</sub><sup>-</sup> for biosynthesis (Hansson and Wydrzynski, 1990) (Eqs. 4 and 5).



PS2 oxidizes water using what is known as the oxygen-evolving centre (OEC). Its active site comprises a CaMn<sub>4</sub>

centre (Dismukes, 2000). At this site the electrons and protons are stripped from the bonded water in the OEC and transferred separately to engender biosynthesis, while the two remaining oxide ions bond covalently to form waste  $O_2$ . To explain such an extraordinary innovation Russell and Hall (2002) suggested that a small cluster, which otherwise would have been interred in the phylломanganate mineral ranciéite  $[CaMn_4^{4+}O_9 \cdot 3H_2O]$ , was co-opted on the outer surface of the membrane of the photosynthetic precursor, and from there sequestered into a protein complex as a “ready-made” catalytic centre. Such phylломanganates (e.g. the birnessites) are produced by hard UV radiation ( $\lambda \sim 225$  nm) from  $Mn^{2+}$ -bearing waters (Anbar and Holland, 1992). They occur widely today in seafloor Mn/Fe nodules as well as in submarine exhalites (Burns and Burns, 1979). In ranciéite the  $Ca^{2+}$  (or a diadochic reduced  $Mn^{2+}$ ) is coordinated with three oxygens as well as to the oxygens of three water molecules (cf. Post and Veblen, 1990; Manceau et al., 2002). However, Ferreira et al. (2004) have now shown that the OEC comprises a cubane containing one Ca atom and three Mn ions. This  $CaMn_3O_4$  cubane is coordinated to a peripheral Mn (Ferreira et al., 2004). Yet the two water molecules are bound between the calcium and the distal manganese. Despite the similar stoichiometry, as the structure of ranciéite does not involve a cubane it could not have been a direct precursor. More in keeping with the Ferreira model are entities of the hollandite  $[(Ba, Mn^{2+})Mn_7^{4+}O_{16}]$  structure favoured by Sauer and Yachandra (2004). Such manganese minerals do readily participate in redox reactions (Sunda et al., 1983; Post, 1999).

In the light of this information, we now imagine the precursors to the cyanobacteria embedded at the top of shallow-water, photolytically precipitated, sedimentary manganese oxides. These precipitates, aptly named umbers when found in more recent oceanic crust (Constantinou and Govett, 1972), not only provided some shade to these precursors, but also contributed the facility to oxidize water, i.e., a “catalase” activity. Here the cyanobacteria precursors exploited the protons and electrons released to them from  $[CaMn_4]$  structures by photons, to reduce bicarbonate ions in pore spaces (Dismukes et al., 2001; Russell et al., 2003). Eventually these  $[CaMn_4]$  molecules with photolytic function were invaginated to become a primitive oxygen evolving complex (OEV). Alternatively, because the adventitious accumulation of  $Mn^{II}$  inside a bacterium afforded strong protection from hard UV and therefore survival, once there it could, along with  $Ca^{2+}$ , have formed a cubane and been chelated by an aspartate- and glutamate-bearing protein. Placed within the membrane, it exerted a water-oxidizing capability. *Deinococcus radiodurans* is known to be tolerant to high doses of gamma-radiation, a tolerance imparted by the accumulation of manganese (Daly et al., 2004). Whatever the details, it does seem likely that this extraordinary innovation, like the emergence of chemosynthetic life itself, also required chemical sediment for protection, support and as a source of metal ions.

### 5.3 The appearance of oxygenic photosynthesis

We do not know when oxygenic photosynthesis started. Did it appear in the Hadean or at the end of the Archaean, over a billion years later? Geochemical evidence from the Isua Banded Iron Formation (Dymek and Klein, 1988), from radio- and stable isotopes in rocks of the same age (Rosling and Frei, 2003), and 16sRNA evolutionary trees (Pace, 2002), have been taken to imply that it emerged before 3.75 Ga. But soil profiles lacking  $Fe^{III}$  and the absence in rocks of the petrified polysaccharide-rich sheaths around fossil cells to be expected of cyanobacteria seem to point to a late or post Archaean age (Westall 2001, 2003, 2004). Indeed, Blank (2004) suggests that oxygenic photosynthesis did not emerge until immediately prior to the Great Oxidation Event at ca. 2.3 Ga (Holland, 2002).

In the absence of further discriminatory evidence our own preference – based on our plate tectonic scenario, the similarity of the oxygen-evolving centre to a hollandite cluster, the rapidity in which dynamic structures evolve and emerge in the Universe, the pedigree of PS2 founded in the antecedent RC2, and the likely concentrations of phylломanganates, as well as of manganese ions in pore waters of littoral sediments – is for the early onset of oxygenic photosynthesis. The absence of atmospheric oxygen prior to 2.3 Ga would then be explained by the flooding of the atmosphere with methane and hydrogen from the deep biosphere, by the buffering effects of reduced iron and sulfide in the ocean and crust, the relatively low productivity in the oceans, and by the reduction of  $O_2$  by ambient bacteria in microbial mats (Lécuyer and Ricard, 1999; Farquar et al., 2000; Hoehler et al., 2001; Catling et al., 2001; Timmins et al., 2001; Bjerrum and Canfield, 2002; Arnold et al., 2004).

## 6 Conclusions

1. Geodynamic and metabolic cycles are closely coupled on our planet, a coupling that would have been even more direct at the onset of life when hydrothermal output from an alkaline submarine seepage of moderate temperature was the input to the first metabolizing systems (Russell and Martin 2004). These “metabolists” developed within catalytic iron sulfide compartments in the hydrothermal mound, gained genetic machinery and thereby evolved while still within the mound. There they differentiated into the two prokaryotic domains, the bacteria and the archaea (Martin and Russell, 2003). It is likely that life had emerged on the planet at least by 4.2 Ga (Russell and Hall, 1997).
2. Gradual expansion of colonies of prokaryotes from the mound into the surrounding sediments on the ocean floor guaranteed a similar protected environment, though nutrient was at a premium, a factor encouraging both syntrophic cooperation and evolution. From here

the colonies were entrained in migrating fluids to depth in the oceanic crust to inaugurate the deep biosphere (Parkes et al., 1990, 1994; Pedersen, 1993; Thorseth et al., 1995). A continual draft of H<sub>2</sub> from the crust and mantle prevented bacterial decay even in periodic absences of an electron acceptor and bicarbonate and other feedstock (Morita, 2000).

3. Because of the relatively low conductivity of mafic rock, the deep biosphere could remain out of reach of meteorite-induced heating events.
4. Obduction of the deep biosphere into the photic zone allowed evolution within shallow water chemical sediments, first of photoprotective molecules developed from aromatic ring compounds previously employed in group and electron transfer, and from these to photosynthetic reaction centres and antenna proteins (Mulikdjanian et al., 1997; Baymann et al., 2001; Allen, 2005).
5. The first photosynthesists, probably precursors of the green sulfur bacteria, used hydrothermal H<sub>2</sub>S as an electron donor and produced S<sup>0</sup> and water as waste. The next, perhaps precursors of the heliobacteria, used organic waste as the ultimate electron donor (Vermaas, 1994). The biggest evolutionary leap followed, and either involved the heterodimerization of the reaction centres of the green sulfur bacteria and the heliobacteria (Bayman et al., 2001), or the divergence of PS1 and PS2 from reaction centres within a green filamentous bacterium (Allen, 2005). Either way a combined cyanobacterial PS1 and PS2 was the result (Blankenship, 2002). This system could oxidize H<sub>2</sub>O leaving O<sub>2</sub> as waste (Dismukes et al., 2001). In doing so, protons and electrons were entrained and used in biosynthesis.
6. Both chemosynthesis and oxygenic photosynthesis emerged within the confines of mineral constituents (iron sulfides and manganese oxides respectively) with catalytic propensity. Molecules that otherwise would have been contributed to the growth of sulfide and oxide minerals were sequestered into the first acetogens and the first oxygen evolving photosynthetic bacteria respectively. Co-opted as vital catalysts, as reactive centres, these transitional metal complexes are employed in the same roles in protein complexes to this day.

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