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The onset and early evolution of life

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ABSTRACT

The tension between CO_2 dissolved at relatively high atmospheric pressure in the Hadean ocean, and H_2 generated as ocean water oxidized ferrous iron during convection in the oceanic crust, was resolved by the onset of life. We suggest that this chemosynthetic life emerged within hydrothermal mounds produced by alkaline solutions of moderate temperature in the relative safety of the deep ocean floor. Exothermic reaction between hydrothermal H_2, $HCOO^-$ and CH_3S^- with CO_2 was catalyzed in inorganic membranes near the mound's surface by mackinawite (FeS) nanocrysts and "ready-made" clusters corresponding to the greigite (Fe_5NiS_8) structure. Such clusters were precursors to the active centers (e.g., the C-cluster, Fe_4NiS_5) of a metalloenzyme that today catalyzes acetate synthesis, viz., the bifunctional dehydrogenase enzyme (ACS/CODH). The water, and some of the acetate ($H_3C.COO^-$), produced in this way were exhaled into the ocean together as fluid waste. Glycine ($^+H_3N.CH_2.COO^-$) and other amino acids, as well as tiny quantities of RNA, generated in the same milieu were trapped within tiny iron sulfide cavities.

Energy from the acetate reaction, augmented by a proton gradient operating through the membrane, was spent polymerizing glycine and other amino acids into short peptides upon the phosphorylated mineral surface. In turn these peptides sequestered, and thereby protected, the catalytically and electrochemically active pyrophosphate and iron/nickel sulfide clusters, from dissolution or crystallization.

Intervention of RNA as a polymerizing agent for amino acids also led to an adventitious, though crude, process of regulating metabolism—a process that was also to provide genetic information to offspring. The fluxes of energy and nutrient available in the hydrothermal mound—commensurate with the requirements of life—encouraged differentiation of the first microbes into two separate domains. At the bifurcation the Bacteria were to specialize in acetogenesis and the Archaea into methanogenesis. Representatives of both these domains left the mound by way of the ocean floor and crust to colonize the deep biosphere.

Once life had emerged and evolved to the extent of being able to reduce nitrogen for use in peptides and nucleic acids, light could have been used directly as an energy source for biosynthesis. Certain bacteria may have been able to do this, where protected from hard UV by a thin coating of chemical sediment produced at a subaerial hot spring operating in an obducted and uplifted portion of the deep biosphere.

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Embedded in fresh manganiferous exhalites, early photosynthetic bacteria could further protect themselves from radiation by adsorbing manganese on the membrane. Organization of the manganese with calcium, within a membrane protein, happened to result in a $CaMn_3O_4$ cluster. In Mn(IV) mode this structure could oxidize two molecules of water, evolve waste oxygen, and gain four electrons and four protons in the process to fix CO_2 for biosynthesis. All these biosynthetic pathways had probably evolved before 3.7 Ga, though the reduced nature of the planet prevented a buildup of free atmospheric oxygen until the early Proterozoic.

Keywords: CODH/ACS, greigite, origin of life, oxygenic photosynthesis, ranciéite.

By *autogeny* we understand the origin of a most simple organic individual in an *inorganic formative fluid,* that is, in a fluid which contains the fundamental substances for the composition of the organism dissolved in simple and loose combinations (for example, carbonic acid, ammonia, binary salts, etc.).

—Ernst Haeckel 1892, p. 414

INTRODUCTION

In a posthumous paper published in 1952, Goldschmidt presented three principles to be adhered to in origin-of-life studies, principles derived from his geochemical and mineralogical experience:

> The **first** principle is that an a-biotic environment, poor in elementary oxygen, is suitable for the preservation and accumulation of ... organic molecules.
>
> The **second** principle is the collection, concentration and ordering of such molecules on free rectilinear planes, crystal faces, of minerals, giving them possibilities for further mutual interaction between themselves and the "basement" crystal.
>
> The **third** principle is the hypothesis that carbon dioxide (and its nearest derivatives) may be the primary material.

These principles, consistent with early geological interpretations of the moderate redox state of the early atmosphere, stand in stark contrast to the assumptions of Oparin (1924, 1938), Haldane (1929), Urey (1952), Oró (1961), Deamer (1985), Joyce (1989), Miller (1992), and Bada (2004) that life originated from the plethora of organic molecules supposedly delivered from space or generated in a putative reduced atmosphere. Goldschmidt, like the evolutionist Haeckel (1892) before him, inferred life to have emerged autogenically (i.e., from the simplest of inorganic substances), whereas Oparin assumed, and his followers assume still, a plasmogenic or organotrophic inheritance to explain their RNA and lipid worlds (Bada, 2004).

In this contribution we develop Goldschmidt's autogenic principles to show that evolutionary steps may be traced, though uncharted in places, mechanistically from aqueous geochemistry and mineralogy, through chemosynthetic biochemistry to oxygenic photosynthesis. The *abiotic environment* we favor for the accumulation and preservation of organic molecules is within FeS microcavities in a submarine hydrothermal mound. The *basement crystals* collecting, concentrating, ordering, and promoting mutual further interactions are the metastable iron sulfides, mackinawite and greigite—sulfides which accommodate that effective and common catalytic metal, nickel. The primary *carbon dioxide*, which composed a proportion of the atmosphere/ocean system (the volatisphere), is fixed by reaction with activated hydrothermal H_2 emanating from the highly reduced Earth to provide the basic organic molecules of life. Hydrogen, as a carrier and donor of high-energy electrons, is the first fuel of life. And as soon as organic molecules are generated they can inhibit crystal growth. Indeed growth of inorganic clusters may be arrested at a very early stage by certain charged or polar organic molecules (Rickard et al., 2001). In some cases these clusters can act as catalysts for further organic synthesis.

Although the potential energy available for reaction between the highly reduced Earth and its moderately oxidized volatisphere is substantial, the kinetic barriers are formidable (Shock, 1992). When hydrothermal solutions first titrated with a sterile prebiotic ocean, much of the thermal energy was effectively dispersed. Not so the chemical energy. Here we attempt to show how a hydrothermal mound at moderate temperature focused and catalyzed the reaction between the main molecules fundamental to life, H_2 and CO_2, and then fractionated, concentrated, and contained the longer charged products. In so doing we rely on the thermodynamic calculations and kinetic considerations of Shock and his collaborators in predicting the likely products of the earliest metabolism (Shock, 1990, 1992; Amend and Shock, 1998; Shock and Schulte 1998; Shock et al., 1998). We also appreciate the operations of Geochemist's Workbench in the presentation of relative stability fields in Pourbaix (Eh/pH) diagrams interpretable by both geochemists and biochemists (Bethke, 1996). Even these geochemical considerations must be given geological context. The emergence of life must be seen as a geological issue, as the first stage in the "evolution of species" and not some separate conception to be examined merely by dismantling a bacterial cell and looking for the oldest bits (Leduc, 1911). And the geochemical reactions must be translatable to an early plausible biochemistry. For example, reactions that make organic polymers

only at temperatures above 200 ºC have little direct bearing on the problem. Life exists as the energy trap and catalyst for reactions between reduced and oxidized components. Like a mineral exploration geologist searching for a lithochemical aureole to an orebody as an indicator of "spent" ore solutions (Russell, 1974), in order to comprehend the process of emergence we have to examine life's waste products, the entropic sinks. Amongst these are the fluid wastes, water, acetate, methane, hydrogen sulfide, and oxygen. These waste products continued to be dispersed, then and now, by convection and advection, albeit at differing rates. The solid mineral wastes, especially the sulfides, are generally deposited close to the source.

So what were the geological and geochemical conditions in the Hadean that gave rise to life and its waste products?

INITIAL CONDITIONS

As soon as the first ocean condensed and cooled around 4.4 Ga Earth was primed for life (Wilde et al., 2001; Russell and Hall, 1997). But where on Earth could life have begun? Conditions were anything but equable. The temperature of the oceans fluctuated wildly. Large meteorites that partially vaporized the ocean increased atmospheric pressure so that the remaining water might have reached 300 ºC or so. In lulls in the bombardment, high CO_2 pressures could induce a 100 ºC greenhouse (Kasting, 1993), yet meteorite-induced dust clouds might, on occasion, have masked radiation from the weak young sun. If so, a short-lived icehouse could have ensued (Nisbet and Sleep, 2001). However, conditions in this "water world" were generally tempestuous; the ocean surface was no place to organize the first cell, and shorelines, where they existed, would have suffered continual storms and huge tides, a response to the closer moon rapidly orbiting about an Earth whose day lasted a mere five hours. Darwin's "warm little pond," if it was not swamped, would have been subject to deleterious hard UV at eight times the present flux (Canuto et al., 1982; Bahcall et al., 2001; Abe and Ooe, 2001). The only safe place to be was on the ocean floor.

Can we imagine a window of opportunity for life to onset? After all, there was no shortage of the appropriate energies, both physical and chemical. Hydrothermal convection currents within the thick, fractured, and permeable Hadean crust focused a chemical disequilibrium between reduced iron (in ferrous minerals and as minor native iron) and the relatively oxidized volatisphere. Although there was chemical potential for reaction between the H_2, continuously emanating from Earth's interior and CO_2 in the atmosphere and ocean, an electrochemical potential between redox couples H^+/H_2 (the hydrothermal state) and Fe^{3+}/Fe^{2+} (the state in the ocean) also obtained.

A geological phenomenon to excite an earth scientist imagining the onset of life is the black smoker (Corliss et al., 1981). Such a very hot spring, emanating at close to the critical point of seawater, is acidic as a result of the serpentinization of pyroxenes at high temperature. In these conditions Mg^{2+} from ocean water in the convective downdrafts is precipitated as brucite ($Mg(OH)_2$) or serpentinite and protons are returned in its stead (Seyfried and Bischoff, 1981; Douville et al., 2002):

$$2MgSiO_3(\text{enstatite}) + Mg^{2+} + 3H_2O \rightarrow Mg_3Si_2O_5(OH)_4\ (\text{serpentine}) + 2H^+ \quad (1)$$

At the same time any sulfate is scrubbed out as magnesium hydroxide sulfate hydrate is produced within the crust, further contributing to the low pH of high-temperature hydrothermal solutions (Bischoff and Seyfried, 1978; Janecky and Seyfried, 1983):

$$2Mg^{2+} + 3H_2O + SO_4^{2-} \rightarrow Mg(OH)_2{:}MgSO_4{:}H_2O + 2H^+ \quad (2)$$

In the near absence of sulfate (equation 2) but with springs exhaling into an acidulous ocean there would have been no anhydrite and sulfide chimneys, and no black smokers in the Hadean. Free sulfide concentrations in the hot fluids were relatively low. The little there was would have reacted with zinc to produce stable ZnS and $Zn_2S_3^-$ clusters (Walker and Brimblecombe, 1985; Luther et al., 1999). Minor to trace quantities of other "biophile" elements such as Mn, Zn, Ni, Co, Mo, Se, and W (Goldschmidt, 1937) would also have been delivered, with iron, to the Hadean ocean through these high temperature springs at oceanic spreading centers (Von Damm, 1990; Hemley et al., 1992). The iron concentrations contributed in this way probably approached 20 mmol. We base this estimate on analyses of the Rainbow hydrothermal system operating in ultramafic rock at the slow spreading Mid-Atlantic Ridge (Douville et al., 2002) (Table 1). Ocean floor spreading in the Hadean was unlikely to have been fast because of the inhibiting effects of a 30-km-thick crust produced by the voluminous melting of a very hot and dry mantle, not to men-

TABLE 1. COMPARISON BETWEEN HIGH AND MODERATE TEMPERATURE SUBMARINE SPRINGS

Parameter	Juan da Fuca	Rainbow	Lost City	Eyjafjordur
T °C	224 °C	365 °C	40°–90 °C	71.4 °C
pH	3.2	2.8	≤11	10.03 (at 24 °C)
H_2	na	13	≤15	na
H_2S	3.5	1.0	0.064	0.01
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_2	23.3	6.9	na	1.6
CO_2	δ4.46	na	na	0.57
SO_4	0	(0)	5.9–12.9	0.2
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
Duration yr	>1000	>1000	>30,000	~11,000

Note: Data from Von Damm, (1990), Douville et al., (2002), Kelley et al., (2001, 2005), Früh-Green et al. (2003), and Marteinsson et al., (2001). Elemental and molecular concentrations are in millimoles. Note that most submarine springs probably last for at least 100,000 years (e.g., Lalou et al., 1993; Früh-Green et al., 2003).

tion the additional tens of kilometers of oceanic volcanic plateaus produced from mantle plumes (Arndt and Chauvel, 1990; Arndt, 1999; Russell and Arndt, 2005) (Fig. 1). And hydrostatic pressures, and thereby temperatures of the hydrothermal fluid, may have been higher in the Hadean because of the deep penetration of fluids to the margins of the crystallizing magma chambers under a deeper ocean. As a consequence, iron concentrations also may have been correspondingly even higher (Von Damm, 2000; Bounama et al., 2001; Allen and Seyfried, 2003).

Although it has been pointed out that temperatures of such hot acidic springs at spreading centers in the Hadean were so high as to destroy organic molecules (Miller and Bada, 1988), they would have provided phosphate, as well as the trace elements that were to help energize and catalyze life, directly to the ocean (Kakegawa et al., 2002).

Given these hydrothermal contributions, what was the state of ocean chemistry? As atmospheric CO_2 of mainly volcanic derivation was at a pressure of anywhere between 0.2 and 10 bars, oceanic pH probably varied between 5 and 6. It could have been higher following major meteorite impacts when large quantities of rock dust were raised to the atmosphere (Nisbet and Sleep, 2001). Rainfall was likely to have been high, but there was little if any atmospheric weathering and runoff because, though there probably were continents, radioactive heating made them plastic and they rarely emerged above the surface of the relatively deep ocean (Sandiford and McLaren, 2002; Russell and Arndt, 2005). However, the iron contributions from the magmatically driven hot springs were diluted by the iron-free submarine alkaline springs exhaling from the ridge flanks and on the deep ocean floor. There were also quantities of ferric oxyhydroxide (FeOOH) particles (denoted by Fe^{III}) produced by photolysis (Cairns-Smith et al., 1992; Russell and Hall, 2002) (Fig. 2A):

$$2Fe^{2+} + 2H^{+} + \text{light} \rightarrow 2Fe^{III}\downarrow + H_2\uparrow \quad (3)$$

Taking account of dilution, photo-oxidation and precipitation, we speculate that the carbonic ocean carried up to 10 mmol of ferrous iron.

The hydrothermal convection cells feeding the alkaline springs were partly driven by exothermic serpentinization, a process that begins slowly at around 85 ºC (Martin and Fyfe, 1970; Wenner and Taylor, 1971). Flow in fractures within the oceanic crust was facilitated partly by geodynamic stresses and partly by the tidal stresses induced by the close and rapidly orbiting moon

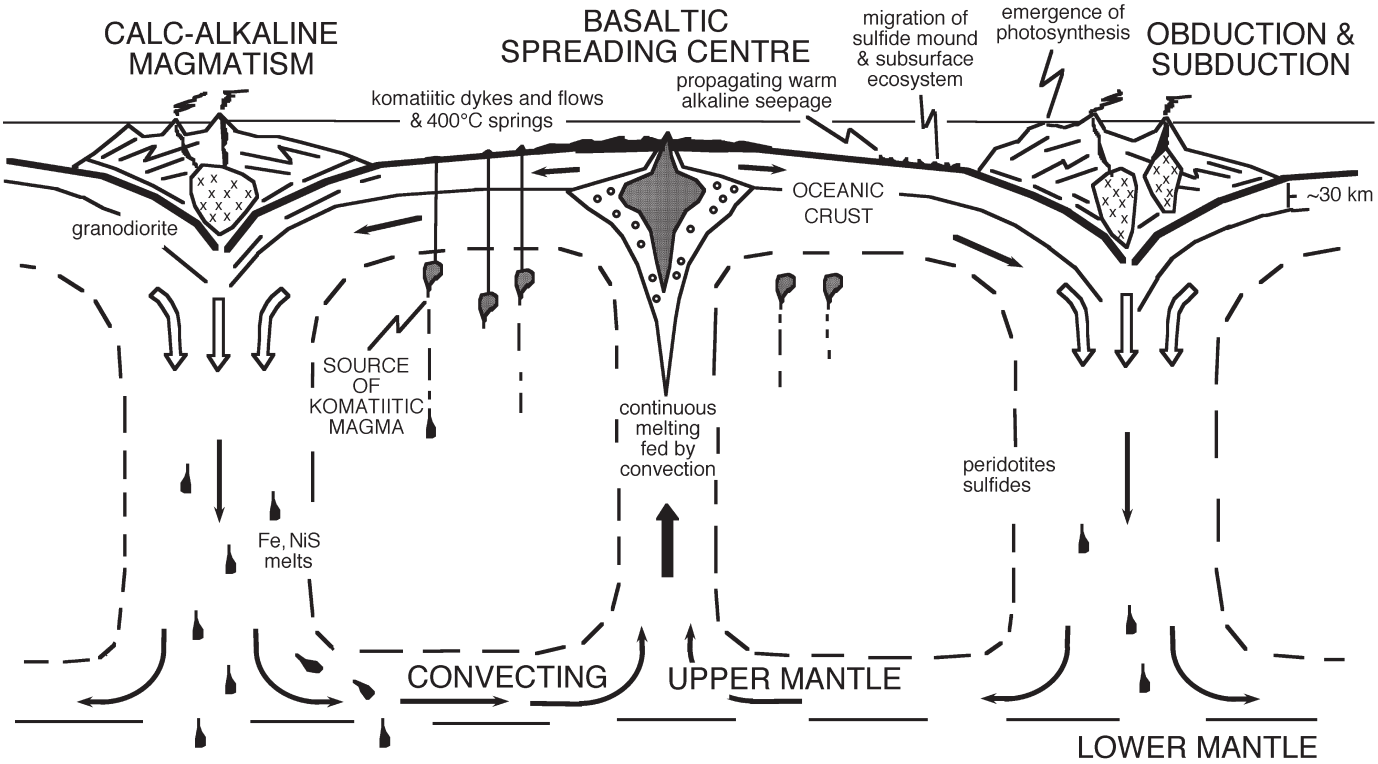

Figure 1. Cross-section of mantle convection cell for Earth at >4 Ga (Smith, 1981; Campbell et al., 1989; Davies, 1992; Karsten et al., 1996; Foley et al., 2003; Russell and Arndt, 2005). Chemosynthetic life emerged at a warm alkaline seepage and expanded into the surrounding sediments and crust, and was conveyed by ocean floor spreading toward a constructive margin produced largely by obduction. Once uplifted at the margin, a proportion of cells invaded sediments in the photic zone where, at a sulfurous spring, some evolved to exploit solar photons. Oxygenic photosynthesis was a further evolutionary development.

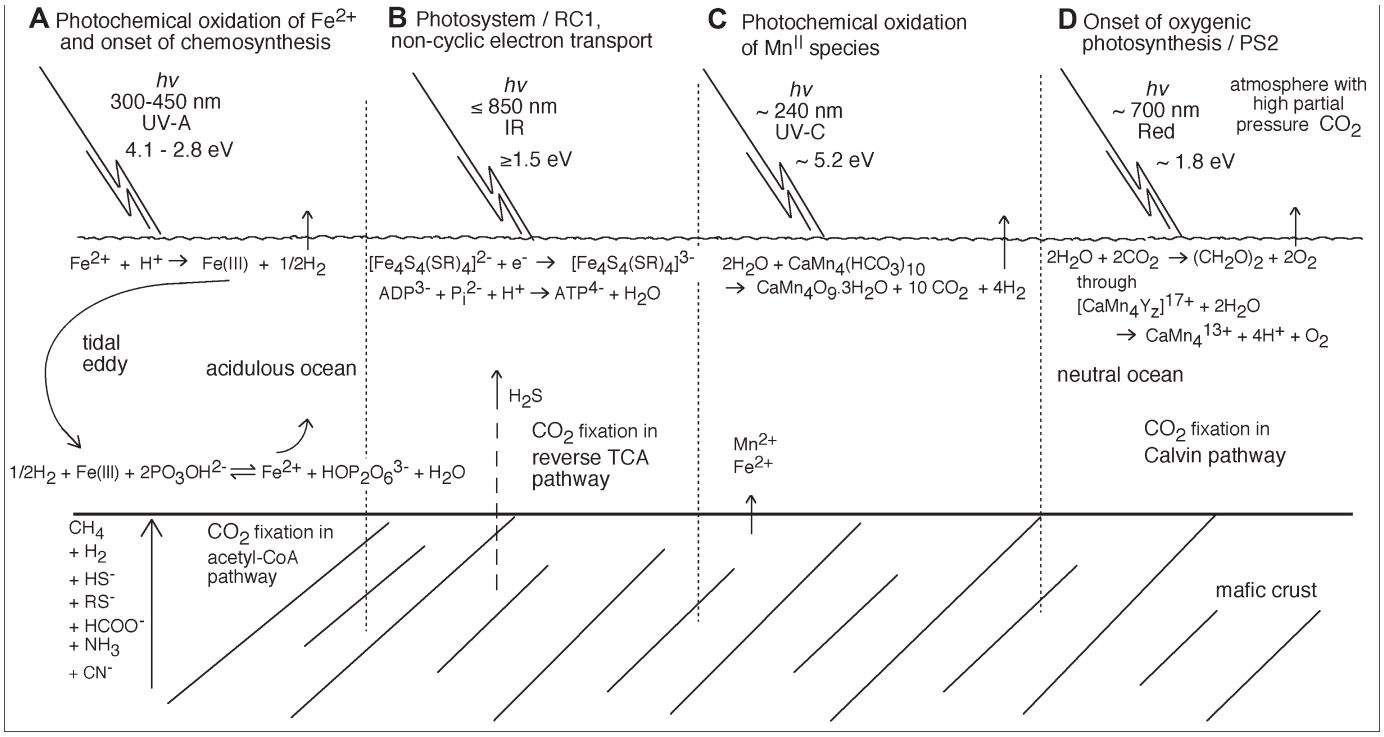

Figure 2. The focusing of solar energy to produce (A) photolytic iron oxidation and the potentiation of chemosynthetic life (Cairns-Smith et al., 1992); (B) reduction of ferredoxin and the onset of photo-induced non-cyclic electron transport (Blankenship, 2002); (C) photo-oxidation of Ca-Mn bicarbonate and generation of a precursor to the water oxidizing complex (Anbar and Holland, 1992; Dismukes et al., 2001; Russell and Hall, 2001, 2002); and (D) oxygenic photosynthesis through reduction of Mn_4^{IV} (Blankenship, 2002). Iron and manganese are exhaled from hot springs at ocean floor spreading centers and at island chains.

(Gaffey, 1997). Nevertheless serpentinization and carbonation may have blocked most fractures at temperatures above ~115 ºC (Wenner and Taylor, 1971).

Although it is well understood that high temperature springs have a pH of between 2 and 3, a consequence of the loss and fixation of Mg^{2+} and the concomitant release of two protons (equations 1 and 2) (Von Damm, 1990; Allen and Seyfried, 2003), less well known is the fact that magnesium is rendered more soluble during the exothermic serpentinization of olivine and pyroxene below 200 °C (Fig. 3) (Macleod et al., 1994; Palandri and Reed, 2004). Because of this, hydroxyl rather than H^+ is generated as a byproduct of the serpentinization:

$$3MgFeSiO_3 + 7H_2O \rightarrow 3SiO_2 + Fe_3O_4 + 3Mg^{2+} + 6OH^- + 4H_2\uparrow \quad (4)$$

Thus these moderate temperature springs are buffered to a pH of 10–11 by the precipitation of brucite [$Mg(OH)_2$] and their temperature may be controlled at ~115 °C (Wenner and Taylor, 1971).

Hydrogen is produced in both the low and high temperature systems on the oxidation, by water, of ferrous-iron-bearing minerals to magnetite (equation 4). Hydrogen will also have been generated on the oxidation of the vestiges of native iron in the Hadean crust (Righter et al., 1997).

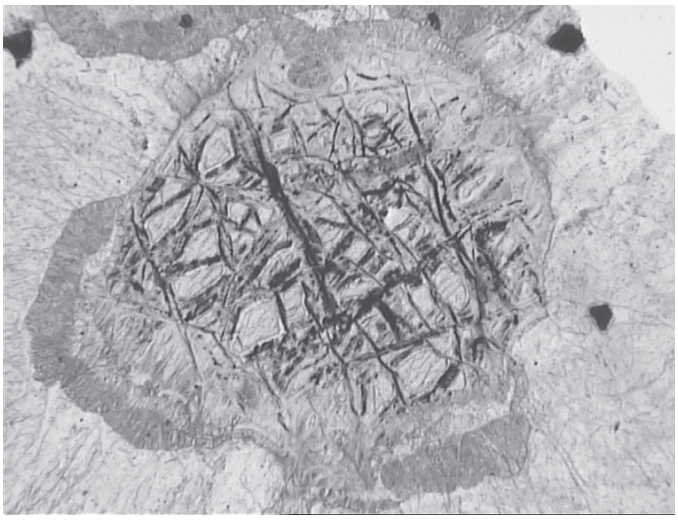

Figure 3. Photomicrograph showing typical texture of a millimetric grain of serpentinized olivine as found in diverse rock types. The process only takes place below 350 °C (Allen and Seyfried, 2003).

$$3Fe^0 + 4H_2O \rightarrow Fe_3O_4 + 4H_2\uparrow \quad (5)$$

Furthermore, reaction with the nickel-iron alloys produced during serpentinization will have released hydrogen to the hydrothermal fluid (Krishnarao, 1964). Other reduced entities likely to be produced in the low temperature alkaline system are ammonia (NH_3), methane thiol (CH_3S^-), hydrosulfide (HS^-), formate ($HCOO^-$), and minor cyanide (CN^-) (Muller, 1995; 995; Russell and Hall, 1997; Shock et al., 1998; McCollom and Seewald, 2003). These molecules provide most of the basic nutrient and

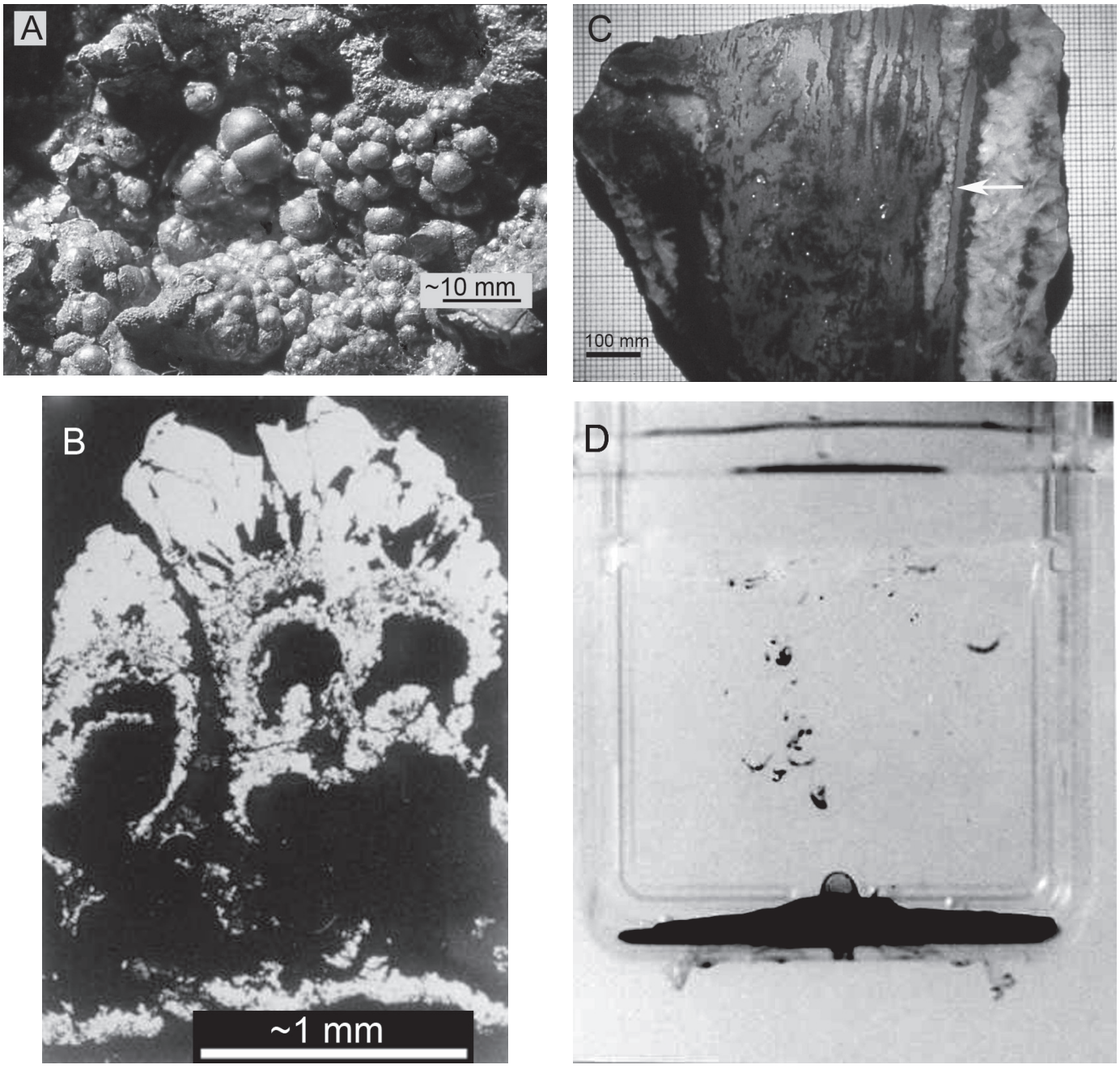

Figure 4. Pyrite botryoids at a 350 Ma fossil warm spring at the Tynagh mine, Ireland: (A) The top surface (field of view measures 2 cm across). (B) Cross-section through pyrite botryoids, revealing bubbles. (C) A natural chemical garden from Tynagh comprising pyrite spires embedded in barite (photographed on centimetric background). (D) Photograph by Martin Beinhorn of a sulfide structure produced as 250 mmol of Na_2S is injected into a 25 mmol $FeCl_2$ solution (field of view measures 4 cm across). (Pyrite is presumed to have replaced iron monosulfide membranes in cases A to C [Banks, 1985; Russell, 1988].)

energy requirements of life. On meeting and mixing with the Hadean ocean, hydrothermal mounds would be formed that seem to us the likely hatcheries of life (Russell and Hall, 1997).

EVIDENCE FOR A LOW TEMPERATURE MOUND

We first assumed (Russell et al., 1988, 1989) that hydrothermal precipitates at an alkaline spring or seepage would result in a porous mound somewhat comparable to the submarine exhalative sulfide constructs at the Tynagh and Silvermines orebodies in Ireland (Fig. 4A–C) (Boyce et al., 1983; Banks, 1985; Banks and Russell, 1992; Samson and Russell, 1987). These were the deposits that first excited our interests in life's emergence (Russell et al., 1988, 1989, 1994). Although the iron sulfide mounds at Tynagh and Silvermines resulted from acidic solutions, originally at ~250 °C and emanating into ~60 °C alkaline brine pools in faulted basins at the bottom of the Mississippian sea ca. 350 Ma, we reasoned that the chemical reactions would just as well result in similar precipitates if the two solutions were inverted (Russell et al., 1989). Observations of the kind of alkaline moderate temperature hydrothermal spring we envisaged (Russell et al., 1989, 1998; Shock, 1992) have been made in 1.5 m.y. old ultramafic oceanic crust, 15 km from the Mid-Atlantic Ridge at the so-called "Lost City" field (Kelley et al., 2001; Früh-Green et al., 2003) (Table 1). Nevertheless, although the solutions here are alkaline as we expected, and carried some H_2, the mounds contrasted significantly with our predictions (Russell et al., 1994; Russell and Hall, 1997).

The large edifices at the Lost City spring are composed mainly of carbonate and brucite [$Mg(OH)_2$], though Kelley et al., (2001) deduce a preoxidation sulfide concentration of ~5 mmol kg^{-1} in the hydrothermal solution. The former presence of a similar <100 °C alkaline spring at a transform fault in the Indian Ocean is also indicated by deposits of finely layered hydrated magnesium silicate (sepiolite) mixed with poorly crystalline Fe-Mn hydroxides (Bonatti et al., 1983). Any original carbonate has been redissolved. Another rather similar deposit, though precipitated from fresh water, has been discovered off the north coast of Iceland (Marteinsson et al., 2001; Geptner et al., 2002) (Table 1). Here cones of Mg-rich clay (saponite) tens of meters high are forming where warm (72 °C) alkaline (pH 10) submarine spring waters exhale into a fjord. Although the cones do offer the kind of porous morphology we expected, no sulfides are recorded (Geptner et al., 2002; Martin and Russell, 2003). Some of the differences between our expectations and the modern submarine springs can be ascribed to contrasting conditions in the Hadean when the crust was more reduced, Fe^{2+} concentrations in the ocean were high, and O_2 was negligible or absent.

In the light of these present-day discoveries how then might we refine our model for the emergence of life? Where the convective up-drafts were vigorous, the alkaline spring waters (pH 10–11, ~100 °C) would have exhaled directly into the acidulous Hadean ocean (pH ~5.5) (Russell et al., 1989; Shock, 1992; Macleod et al., 1994; Russell, 2003). We have assumed that at times when solar radiation was masked, this ocean was ~20 °C or less (Fig. 5). Precipitation at the exhalative center was rapid, but

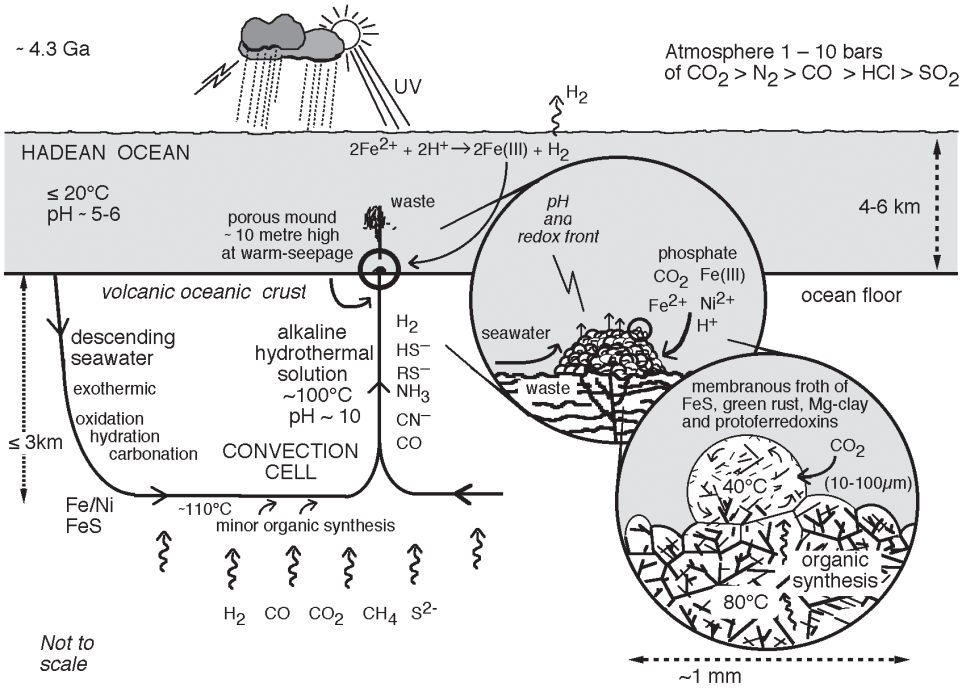

Figure 5. Model environment for the emergence of life at a submarine seepage on the ocean floor (after Russell and Hall, 1997).

as the fracture conduits in the mounds became fouled with carbonate, and with gels and microcrysts composed of silica, sepiolite, saponite, brucite, green rust, and iron sulfide, the fluid egress became diffuse and seepages replaced springs. Such restraint in the seepage mound favored—depending on solutes and local pH—development of siderite, ferrous hydroxide, and/or iron (nickel) monosulfides. What might the structure of these precipitates have looked like?

We originally imagined iron sulfide structures to have precipitated spontaneously at the interface of the hot alkaline seepage waters containing millimoles of HS^- and H_2 with the cool carbonic ocean water bearing millimoles of Fe^{2+} and particulate FeOOH (Figs. 6A, 6B). Our attempts to reproduce similar structures in the lab were relatively successful, though rather high concentrations of HS^- (250 mmol) were required to produce bubbles (Fig. 4D) (Russell, 1988; Russell et al., 1989). Depend-

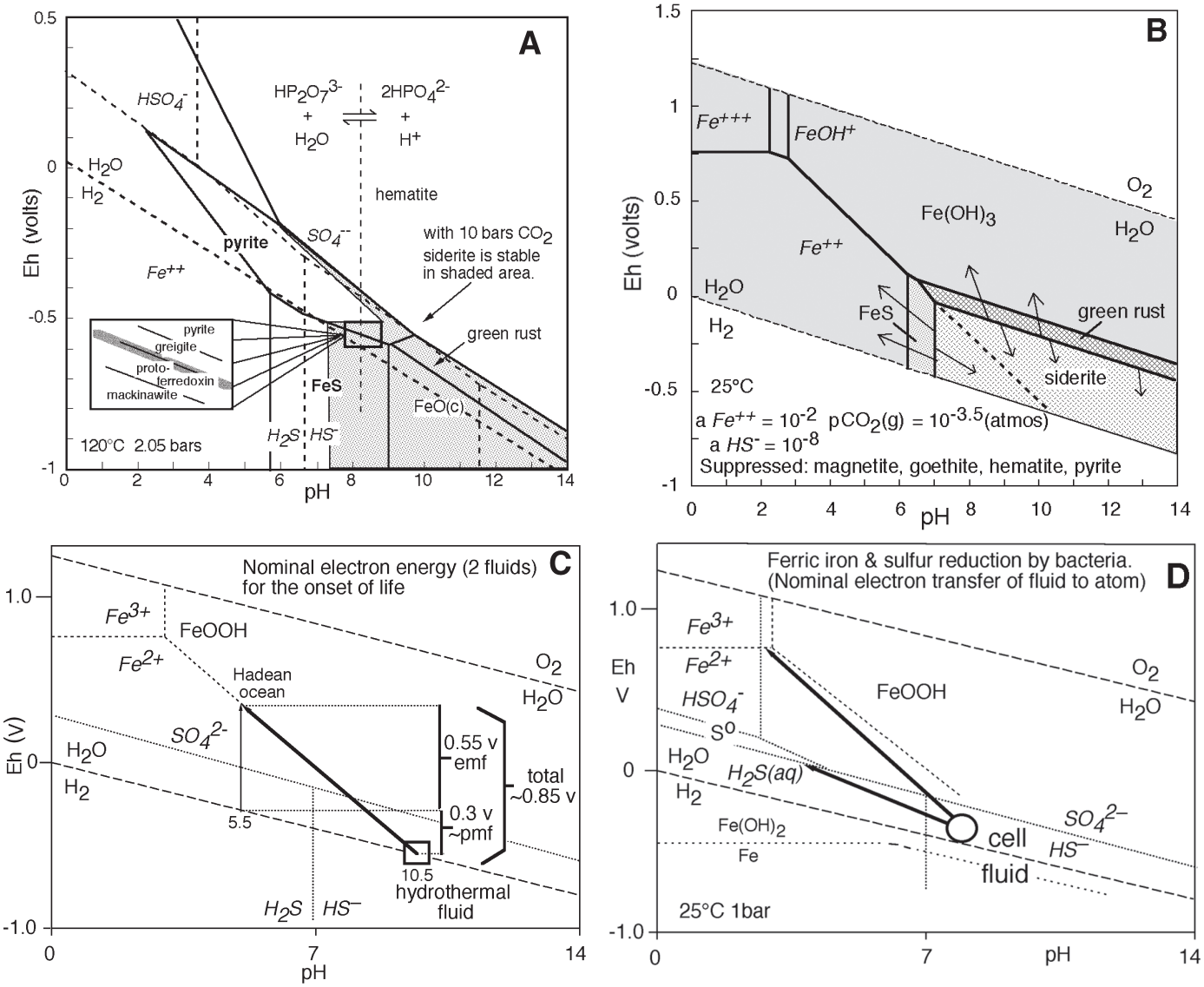

Figure 6. (A) A Pourbaix (Eh/pH) diagram illustrating the stabilities of siderite, mackinawite (as FeS), protoferredoxin, greigite, pyrite, green rust, and hematite, produced for activities of $H_2S(aq) = 10^{-3}$, and $Fe^{2+} = 10^{-6}$, using GWB (Bethke, 1996). The inset shows notional phase relations emphasizing the intermediate oxidation state of the FeS component of membrane protoferredoxins and is positioned to indicate the Eh-pH conditions pertaining to alkaline hydrothermal fluid as it enters Hadean seawater. Note that the pH boundary of monophosphate/polyphosphate intersects this redox position (and see Fig. 16). (B) An Eh-pH diagram computed for modern atmospheric CO_2. At higher pCO_2 the siderite field would expand as indicated by arrows, at the expense of FeS. Such a release of HS^- from pyrrhotite accumulations in the crust to the hydrothermal solution would, on meeting Fe^{2+} within the growing mound, reprecipitate as FeS (Hall et al., 1994). The $Fe^{2+}/Fe(OH)_3$ boundary is projected (dashed line to show its approximate position at very low pCO_2. Calculated using GWB (Bethke, 1996). (C) An Eh/pH diagram illustrating the electrochemical energy potentiating the onset of life and the first microbe. (D) The electrochemical energy available to modern iron reducing bacteria (Zachara et al., 2002) compared with that available from the reduction of native sulfur. After Russell and Hall (1997).

ing on the pH, precipitation of mackinawite [$(Fe>Ni)_{1+x}S$] and green rust [$Fe^{II}_4Fe^{III}_2(OH)_{12}.CO_3^{2-}.2H_2O$] produced chemical gardens comparable to those found at Tynagh (Fig. 4C) (Russell, 1988). Greigite [Fe_3S_4] also occurred, as did violarite [$Fe_2Ni_4S_8$] if Ni^{2+}:Fe^{2+} ratios were high (Russell, 1988; Russell et al., 1998). Mackinawite nanocrysts were probably the main components of the chemical garden and of the membranous walls to individual compartments. We suggest bubbles like these, or at least microcavities within a mackinawite precipitate, acted as the original catalytic culture chambers for early metabolism and embryonic life. Described thus, the hydrothermal mound begins to take on the attributes of a natural catalytic flow reactor and fractionation column and we now examine it in this light (Russell et al., 2003; Stone and Goldstein, 2004; Russell and Martin, 2004).

MACKINAWITE—MEMBRANE MINERAL, PREBIOTIC CATALYST, AND ELECTRON TRANSFER AGENT

Mackinawite provided the inorganic structure and reaction surfaces of the first membrane. At the molecular level mackinawite ($Fe_{1+x}S$) comprises layers of offset Fe_2S_2 rhombs (Wolthers et al., 2003). At the atomic level it can be seen that the iron layers in mackinawite are semiconducting (Vaughan and Ridout, 1971) (Fig. 7), yet across the layers the van der Waals bonding of the sulfurs confers an insulating capacity to the mineral. The particle sizes of the mackinawite precipitates are bimodal—one is 2 × 2 × 1.5 nm (at pH 8), the other 7 × 7 × 3 nm (at pH 6) (Wolthers et al., 2003).

Aided by the electrochemical gradients obtaining near the mound's surface, one of the effects of the inorganic membrane would have been to split hydrogen into electrons, protons, and transient activated hydrogen atoms. We imagine electrons transferring from one semiconducting nanocrystal to the next through the membrane as they were drawn toward external Fe^{III} and/or HCO_3^- within the membrane (Fig. 8). To maintain charge balance the protons were forced to follow by rotational/translational diffusion of water/hydronium molecules that adhered to the crystallite surfaces (da Silva and Williams, 1991, p. 103). As we shall see, the addition of further protons to the exterior of the FeS compartments would have augmented the natural protonmotive force acting on the membrane.

Divalent metal ions can also invade the sulfur layer (Fig. 7), and nickel and minor cobalt as well as other metals can replace iron in the metallic layer. Also mackinawite is potentially a major temporary sink for many trace metals in anoxic conditions, even calcium (Morse and Arakaki, 1993). Morse and Arakaki (1993) demonstrate that the surface affinity of mackinawite during adsorption of Mn^{2+}, Cr^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Cu^{2+} is in the order of their decreasing solubility as sulfides. When taken in conjunction with their high surface-to-volume ratios, mackinawite nanocrysts have excellent catalytic properties (Cody, 2004; Cody et al., 2004). And as we would expect of a catalyst, mackinawite is a highly reactive mineral prone to oxidation. In an anaerobic environment it can be oxidized in two ways. Oxidized by Fe^{3+}, it converts to greigite by loss of electrons from, and reorganization and even some dissolution of, the iron (Krupp, 1994) (Figs. 7, 9A). So we expect greigite to be a minor phase,

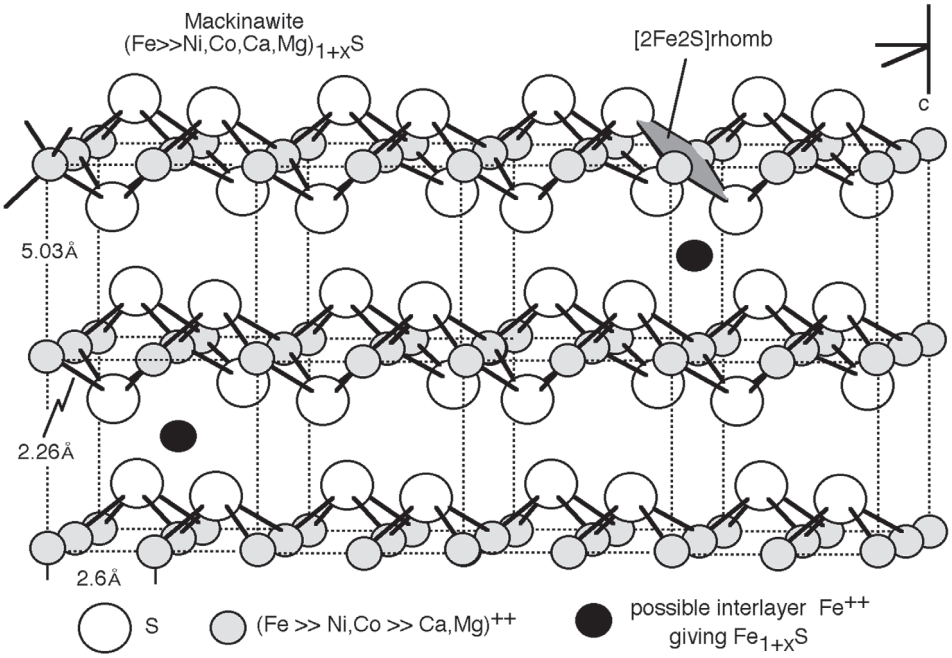

Figure 7. Structure of mackinawite $Fe_{1+x}S$. Mackinawite consists of an assemblage of [2Fe2S] rhombs (Wolthers et al., 2003) arranged in such a way that it acts as a semiconductor in the bc plane and an insulator through the c axis. Comprising the membrane, mackinawite nanocrysts may have acted as the first electron transfer agents from the interior of the protocells to Fe^{III}, the exterior electron acceptor (Fig. 8) (Russell and Hall, 1997; Russell et al., 1998; cf. Ferris et al., 1992).

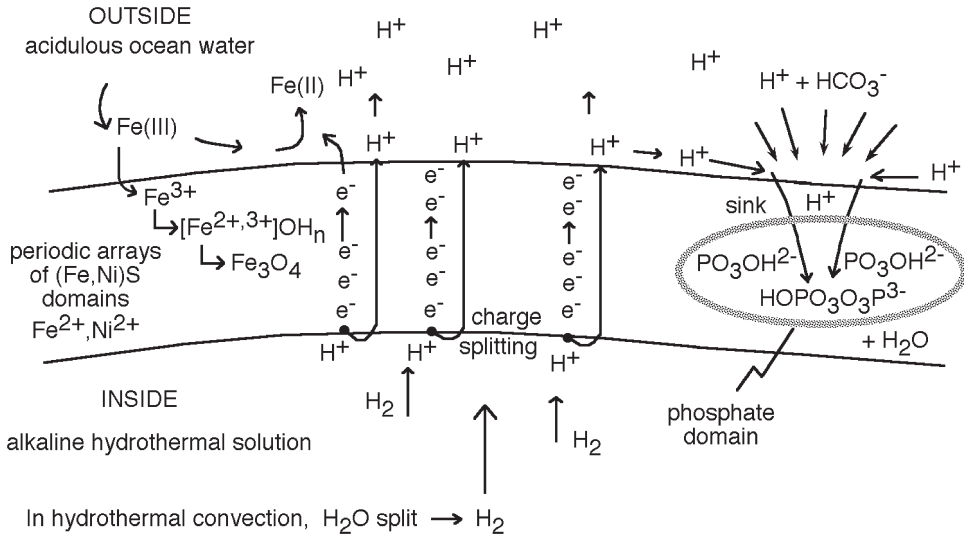

Figure 8. Supposed emergence of chemiosmosis driven by reduction of Fe^{III} on the exterior of the FeS membrane. Electrons are conducted through mackinawite nanocrysts from H_2 oxidized on the interior (cf. Ferris et al., 1992). Protons track electrons through aqueous films by rotational/translational diffusion of H_3O^+/H_2O molecules adhering to the crystallite surfaces (da Silva and Williams, 1991, p. 103) to conserve charge balance. Elsewhere mackinawite may act as an insulator (Fig. 7). The membrane potential is augmented by protons in the acidulous ocean—an ambient protonmotive force.

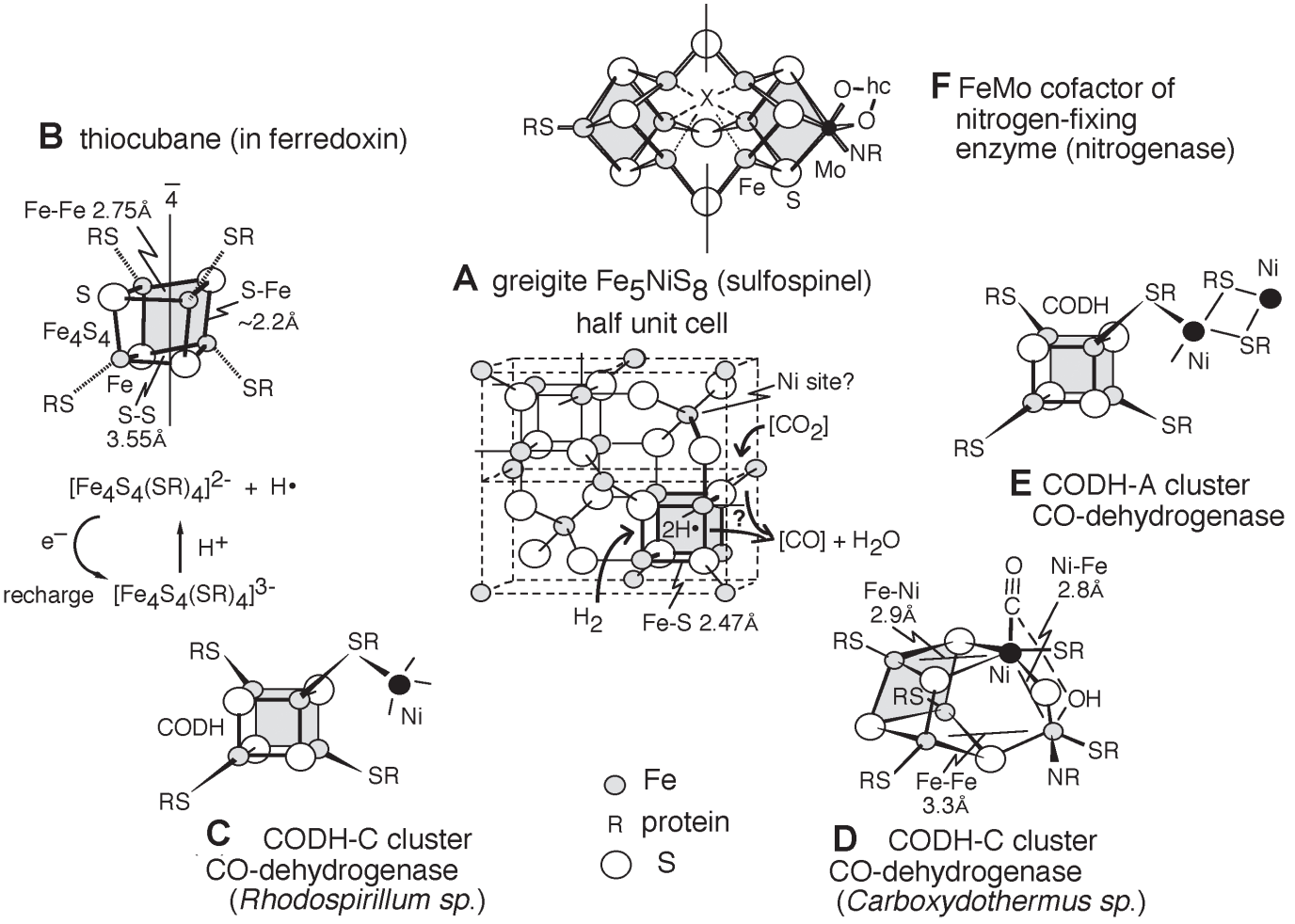

Figure 9. Structural relatedness of (A) greigite Fe_5NiS_8; (B) the thiocubane $[Fe_4S_4]$ unit in protoferredoxins and ferredoxins; (C–E) the $[Fe_4NiS_5]$ open cuboidal complexes in CO-dehydrogenase; and (F) the twinned center to nitrogenase. Affine sulfur sub-lattices, cubic close-packed in A, are distorted in the metalloenzyme centers. The presence or absence of $Fe^{III/3+}$, Mo, Ni, and organic ligands may dictate which of these entities formed in the first cells. RS denotes a link to the protein through the sulfur of cysteine, HN involves a link through a nitrogen ligand of histidine to the same protein, while hc is homocitrate ($^-OOC.CH_2.COH.COO^-.CH_2.COO^-$). Structure (A) from Vaughan and Craig (1978), Krupp, 1994; (B) Hall et al. (1971), Beinert et al. (1997); (C) Drennan et al. (2001); (D) Dobbek et al. (2001); (E) Doukov et al. (2002), Darnault et al. (2003); Svetlitchnyi et al. (2004); (F) Helz et al. (1996), Einsle et al. (2002), Seefeldt et al. (2004).

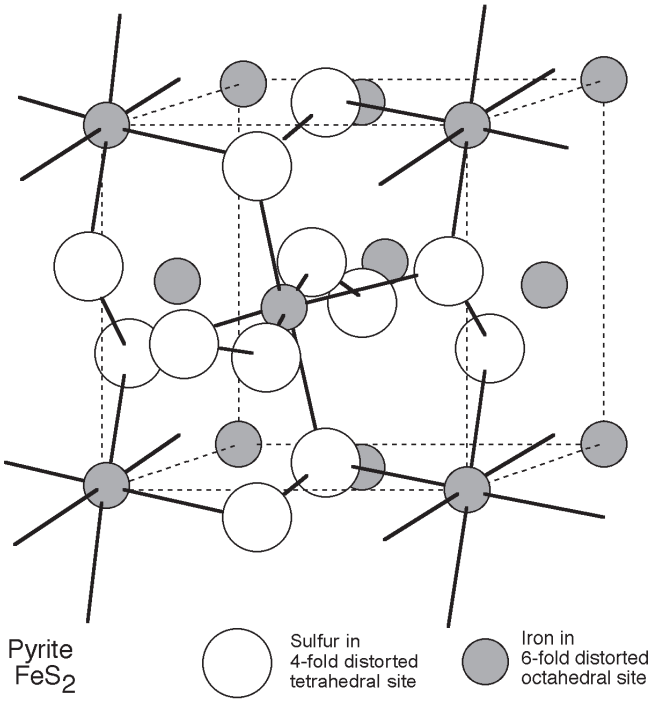

Figure 10. Atomic structure of pyrite drawn to show the ferrous iron ligated to six sulfur-pairs, $Fe^{2+}(S_2^{2-})_6$. The complex structure makes the mineral difficult to nucleate, and difficult to reduce (Finklea et al., 1976) unlike the iron sulfide clusters of metal enzymes (cf. Fig. 9).

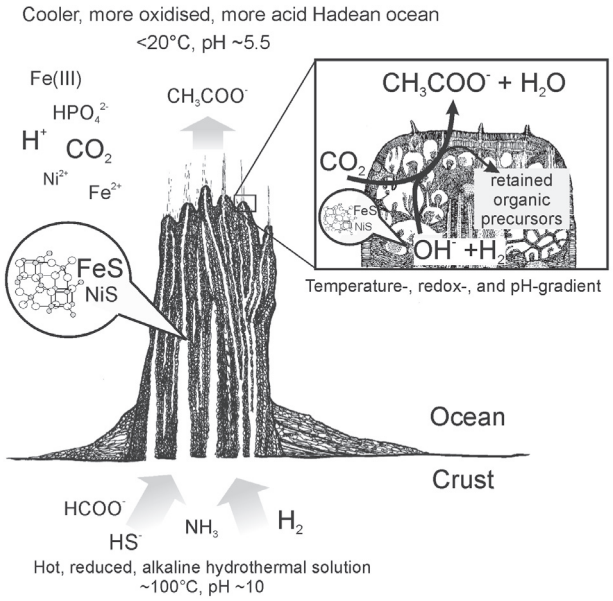

Figure 11. The hydrothermal mound as an acetate generator. The detailed cross-section of the surface illustrates the sites where organic ions are produced, retained, react, and self-organize to emerge as protolife (from Russell and Martin, 2004).

particularly toward the outer margins of the membrane (see next section). Further oxidation converts it to the relatively inert pyrite (Fig. 10). In this latter case it is the sulfur that is oxidized (to S_2^{2-}). Rickard et al. (2001) have shown that this stage of oxidation is prevented by formaldehyde, significant because, as we shall see below, greigite has a structural affinity to ancient metalloenzymes (Fig. 9).

HYDROTHERMAL MOUND AS REACTOR AND ACETATE WASTE GENERATOR

Acting as a natural flow reactor and fractionation column, the hydrothermal mound stood vertically and was composed essentially of brucite, clay, minor sulfides, green rust, and ephemeral carbonate (Fig. 11). Hydrothermal fluid entered through the permeable and porous base. The bubbles and pores stemmed the flow of "electron-rich" molecules such as H_2, NH_3, $HCOO^-$, CN^-, CH_3S^-, and HS^-. The H_2, HS^-, $HCOO^-$ and NH_3 were the most concentrated at 10 or so mmol. This hydrothermal solution mixed with about 100 mmol of HCO_3^- and several millimoles of Fe^{2+} and $HP_2O_7^{3-}/HPO_3^{2-}$ in ocean water that was entrained through the sides of the mound. The HS^- reacted with Fe^{2+} and Fe^{II} (i.e., fixed ferrous iron) to precipitate nickeliferous mackinawite:

$$Fe(Ni)^{2+} + HS^- \rightarrow Fe(Ni)S + H^+ \quad (6)$$

Fresh sulfide nanoparticles acted as sites of adsorption, absorption, and catalysis. Ferric iron particles attracted to the outside of the membrane may have oxidized some of the mackinawite to greigite and even pyrite. Cyanide would have fractionated from the formaldehyde, the former adsorbed on the pyrite, the latter upon the mackinawite (Leja, 1982; Rickard et al., 2001). In places membranes and barriers composed of mackinawite and minor greigite acted as solid phases for further chemical interactions between the reactive solutes (Russell et al., 1994, 2003; Schoofs et al., 2000). What might these reactions have been?

The reaction expected to have released the most energy, i.e., with the greatest thermodynamic drive, was the production of methane and water from the carbon dioxide and the hydrogen (Amend and Shock, 2001):

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (7)$$

However, there is a major kinetic barrier that faces this reaction, which takes place spontaneously only above 500 °C (Shock et al., 1998). The reaction to produce acetate dissipates less energy, but the kinetic barrier is also lower, though not low enough for H_2 to react spontaneously with the CO_2 (Shock et al., 1998; Amend and Shock, 2001). Shock et al. (1998) calculate that carbon in metastable equilibrium states obtained by mixing hydrothermal fluids with anoxygenic seawater below 110 °C would be mainly as acetate, with subsidiary propanate and dodecanoate (Fig. 12). Therefore, we expect the hydrothermal mound and its compartments to have catalyzed the production of acetate (CH_3COO^-) and water from CO_2 (as bicarbonate, Fig. 13) and H_2 below 50 °C, degrading energy in the process (Russell and Martin, 2004):

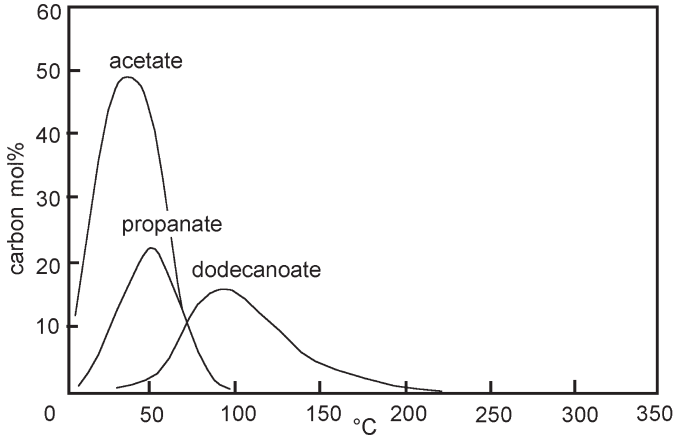

Figure 12. Mole percent distribution of the three most "metastable" carboxylic acids at low to moderate temperatures theoretically obtained through the mixing of hydrothermal fluids with anoxygenic seawater. They are acetate ($CH_3.COO^-$), propanate ($CH_3.CH_2.COO^-$), and dodecanoate ($CH_3.(CH_2)_{10}.COO^-$). (Minor species have been neglected in this redrawing of part of Figure 5.7 in Shock et al., 1998.)

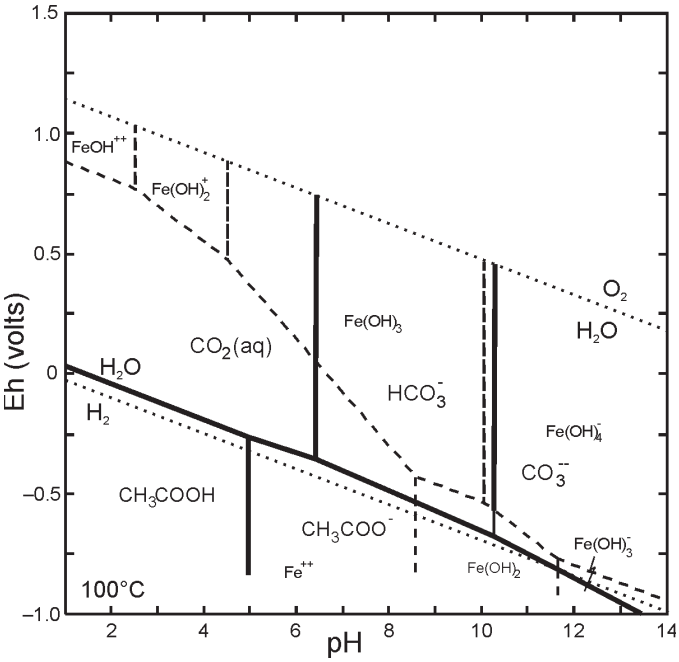

Figure 13. Pourbaix diagram using Geochemist's Workbench ACT2 (Bethke, 1996) showing the acetate and carbonate fields (thick lines) with respect to dissolved and solid iron phases (dashed lines). Conditions: 100 °C, p = 1.013 bars, CO_2(g) log f-3, Fe^{2+} log a-20, fields extended below stability field of water (dotted lines).

$$4HCO_3^- + 8H_2 + 2H^+ \rightarrow 2CH_3.COO^- + 8H_2O \qquad (8)$$

There is some experimental evidence to support the conclusions of Shock et al. (1998). Reacting 100 mmol CH_3SH (methane thiol) and 4.5 mmol CO at 100 °C at normal pressure, Huber and Wächtershäuser (1997) produced micromolar amounts of methyl thioacetate (CH_3COSCH_3) in the presence of an FeS/NiS slurry optimally at pH 6.4:

$$CO + 2CH_3SH \rightarrow CH_3.COSCH_3 + H_2S \qquad (9)$$

Methane thiol has been synthesized from CO_2 at 100 °C in the presence of FeS and H_2S (Heinen and Lauwers, 1996, 1997). At the same time, the FeS was oxidized to pyrite, as might be expected from the "pyrite-pulled" model of Wächtershäuser, 1988). The yield with respect to H_2S was ~0.25%. In theory methane thiol activities would rise a thousandfold when generated from H_2 and CO (rather than CO_2) in the crust or the hydrothermal mound (Schulte and Rogers, 2004). These conditions would have been met within the mackinawitic membrane that separated ocean water at about pH 5.5 from the more alkaline hydrothermal fluids that contained CO and organic sulfides, i.e., the thiols (Russell and Hall, 1997). Hydrolysis would have liberated a proportion of the acetate while the methane thiol catalyst was returned to the solution:

$$CH_3.COSCH_3 + OH^- \rightarrow CH_3.COO^- + CH_3SH \qquad (10)$$

The acetate reaction, augmented by the proton gradient operating across the membrane, may also have been coupled to pyrophosphate generation. (Currently this process is driven by a sodium gradient.) The surviving methyl acetate became involved in further biosynthetic reactions such as the generation of amino acids and lipids. Can we generalize the first evolutionary step?

The notional hydrothermal reactor works to the rule of the second law of thermodynamics. For the most part, we might expect that geochemicals far from equilibrium would react irreversibly, degrading energy in the process (Shock et al., 1998). Minerals such as mackinawite form exothermically on reaction between hydrothermal HS^- and the Fe^{2+} in the entrained ocean water (equation 6), so we can consider the onset of life as similarly exothermic overall and suggest a simplified equation as a demonstration:

$$\{407H_2+10NH_3+HS^-\}_{\text{hydrothermal}} + \{210CO_2+H_2PO_4^- + Fe,Ni,Co,Zn,Mo^{2+}\}_{\text{ocean}} \rightarrow \{C_{70}H_{129}O_{65}N_{10}P(Fe,Ni,Co,Zn,Mo)S\}_{\text{proto-life}} + \{70H_3C.COOH+219H_2O\}_{\text{waste}} \qquad (11)$$

The ratio of waste acetate plus water to "proto-life" in this conceptual reaction is high. Most of the output from the reacting monomers elutes to the ocean and entropy thus increases, but the iron sulfide botryoids, bubbles, and pores could act, albeit inefficiently at first, as tiny electrically powered compartments or "tureens" in which a "warm organic soup" could have been synthesized, constrained and concentrated to a critical mass that encouraged further interactions (Russell et al., 1988, 1994; Braun and Libchaber, 2004). Thus, within the compartments processes

were reversible, and though entropy was exported, it decreased within the compartments themselves (Prigogine, 1978).

This approach does correspond to what is understood of early life from microbiology: many microbes, including those near the base of the evolutionary tree, can gain energy by generating acetate using the enzyme carbon monoxide dehydrogenase with acetyl-coenzyme-A (which is also an organic sulfide or thiol, co-A.SH), through the acetyl-coenzyme-A pathway, that is in part homologous with the Huber-Wächtershäuser reaction (equation 9) (Schink, 1997; Peretó et al., 1999; Amend and Shock, 2001; Russell and Martin, 2004):

$$2CO_2 + 8[H] + \text{co-A.SH} \rightarrow \text{co-A.S.OC.CH}_3 + 3H_2O \quad (12)$$

A portion of the acetate and the energy released in these exergonic reactions would have gone to waste. But waste, the generation of entropy, is life's raison d'être. We might think of the mound as optimizing the generation of acetate over time while side reactions, including many involving the activated thioacetate ($CH_3.COS^-$), synthesized the more complex molecules that interacted to produce life. This non-vivocentric view is now examined in the context of a notional reactor that produces the acetate and water (Figs. 11–13).

Bubbles comprising the iron sulfide membrane could have been hydraulically inflated over warm seepages, where they encapsulated the reduced alkaline hydrothermal solution (Fig. 4D) (Russell et al., 1989, 1993). As the bubbles became distended they weakened, failed, and daughter bubbles were generated above the punctures (Fig. 4B). Thus the redox and pH front remained at the growing surface of the mound (Figs. 4D, 5, 11). Bubbles farthest from the feeder veins would have been disadvantaged unless the structure of their membranes particularly disposed them to supporting an osmotic pressure. This osmotic pressure would have been induced by the generation of abiotic charged organic molecules. Contiguous compartments (Fig. 5), generated by budding of the iron monosulfide membrane (Fig. 4B), would have contained fluid mixes at slightly different Eh and pH conditions and therefore would have harbored different reactants and products, as energy cascaded from one chemical and electrochemical level to another. These possibilities have been elegantly considered for other types of inorganic membrane by Cairns-Smith (1982, p. 327 and 351–356). As discussed below, organic synthesis would have been catalyzed by the iron (nickel) monosulfide, which, unlike fine metal and oxide/hydroxide catalysts, cannot be poisoned by sulfidation.

Although acetate and water were the main fluid products, the hydrothermal NH_3 and minor CN^- would have reacted with bicarbonate on mineral surfaces and produced amino acids, especially glycine ($^+H_3N.CH_2.COO^-$) (Hennet et al., 1992):

$$3CO_2 + 5H_2 + NH_3 + HCN \rightarrow 2(^+H_3N.CH_2.COO^-) + 2H_2O \quad (13)$$

The amino acids were mostly adsorbed within compartments in the mound. With the addition of formaldehyde (HCHO), minor concentrations of RNA would also have been produced from these components (Ferris and Hagan, 1984).

Apart from the fluid wastes, mainly water and acetate, there is also the solid waste product to consider.

PYRITE—A SOLID WASTE PRODUCT

When mackinawite or greigite is oxidized to pyrite, for example during the generation of methane thiol, the rhombic [Fe_2S_2] building block is lost; instead, the ferrous iron is ligated to six partially oxidized sulfur-pairs (S_2^{2-}) (Fig. 10). The resulting $Fe(S_2^{2-})_6$ is a complex structure which makes the mineral difficult to nucleate and very difficult to reduce back to FeS (Finklea et al., 1976). Wächtershäuser (1988) has argued for the formation of pyrite on oxidation of FeS by hydrogen sulfide, with the generation of hydrogen, as the primeval energy source for the origin of a (surface) metabolist. Although we consider hydrogen to be delivered to the mound in the alkaline solution, the Wächtershäuser reaction works in acidic and neutral conditions (Taylor et al., 1979; Drobner et al., 1990; Rickard, 1997). Moreover, the hydrophobic pyrite precipitate recorded at the gas-water boundary in the experiments of Heinen and Lauwers (1996) demonstrates that this irreversible (i.e., non-catalytic) oxidation can drive reductions of CO_2 as suggested by Wächtershäuser (1988). Although this reaction produces less energy in alkaline conditions, were pyrite to have been formed it could have taken no further part in protometabolism and must, therefore, be considered as a waste product. Nevertheless, its hydrophobic surfaces would have rendered it a surficial trap for organic molecules and cyanide gleaned from the hydrothermal fluid (Leja, 1982; Russell et al., 1988).

ENERGY FOR POLYMERIZATION

Although we note empirically that the thermal gradient responsible for convection lies between 115° and <20 °C, the electrochemical potential to drive biosynthesis and polymerization could be subscribed by the H^+/H_2 couple (effectively the hydrogen electrode) representing the hydrothermal emanations, as against the Fe^{3+}/Fe^{2+} couple representing the photolytic ferric iron (representing an initially dispersed positive electrode). Theoretically the hydrothermal hydrogen could have reduced ferric oxyhydroxide (signified as Fe^{III}) to ferrous ions, and produced protons in a reversal of equation 3 in which the redox potential was influenced by light energy:

$$H_2 + 2Fe^{III} \rightarrow 2H^+ + 2Fe^{2+} \quad (14)$$

Pourbaix diagrams idealize the thermodynamic potentials on proton activity (pH) and electron activity (Eh) coordinates (Fig. 6). Oxidation of H_2 on one side of the membrane by reduction, through electron transfer, of Fe^{III} on the other side of the membrane, theoretically generates a potential of 770 mV (Fig. 6C)

(Russell et al., 2003). Other species such a $Fe(OH)_3$ have lower redox potentials, for example $Fe(OH)_3/Fe(OH)_2$ = 270 mV (Garrels and Christ, 1965, p. 183). Even this potential is more than the 250 mV (–11.5 kcal per mole) required to drive polymerization, especially when the pH gradient is taken into account (Thauer et al., 1977; and see Kell, 1988, Van Walraven et al., 1997). This chemiosmotic proton potential is augmented by proton potential of the acidulous ocean (pH ~5.5 at ~20 °C) acting across the inorganic membrane on the alkaline hydrothermal solution (pH ~10.5 at ~100 °C), a potential that results in a further 300 mV (Fig. 6C). *Geobacter metallireducens*, as well as many other bacteria in the lowest branches of the evolutionary tree, can reduce Fe^{III} using much the same electrochemical potential (Fig. 6D, 14) (Liu et al., 1997; Vargas et al., 1998; Zachara et al., 2002).

In sum, the overall "protonic" potential approximates 1 V, enough geochemical energy to have engendered metabolism across an inorganic membrane on early Earth (Russell et al., 2003). Using a "Beutner rig" (Beutner, 1913, Fig. 1), we have found that a spontaneously generated FeS membrane, formed on reaction between 10 mmol solutions of $FeSO_4$ and Na_2S (at pH 4.12 and 10.0 respectively), creates a tension of ~600 mV, which is held for several hours (Fig. 15). Filtness et al. (2003), using more fastidious conditions obtain a total tension closer to 700 mV, differences maintained for more than 4 h. That the pH-dependent boundary between the mono- and di-phosphate fields intersects the (primarily) Eh-dependent iron sulfide fields demonstrates how "proticity" (a proton current) could have driven the condensation of inorganic phosphate (Pi) to pyrophosphate (PPi) (Fig. 16). So in theory the redox reaction outlined in equation 3 could have been simply coupled through the membrane to

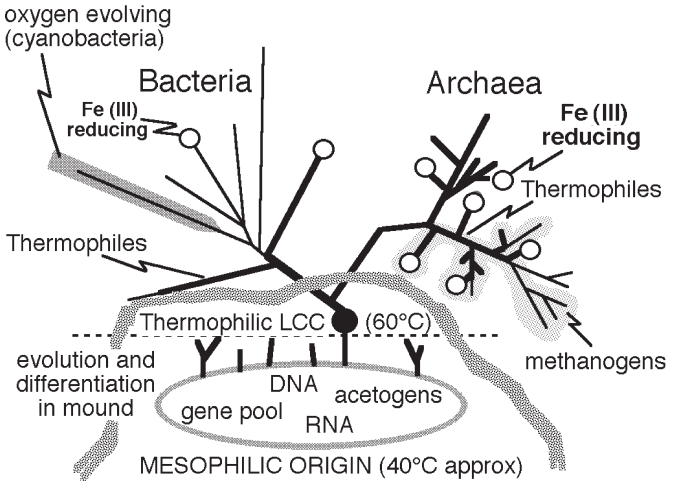

Figure 14. Evolutionary tree (after Woese et al., 1990; Stetter, 1996; Martin and Russell, 2003). The last common community (the LCC) occupied the mound in which life had emerged. Many prokaryotes in the lowest branches of the tree can use Fe^{III} as an electron acceptor (Liu et al., 1997; Vargas et al., 1998; Kashefi et al., 2002). Note that methanogens are found only in the Archaeal domain and that oxygenic photosynthesis is a property only of the cyanobacteria.

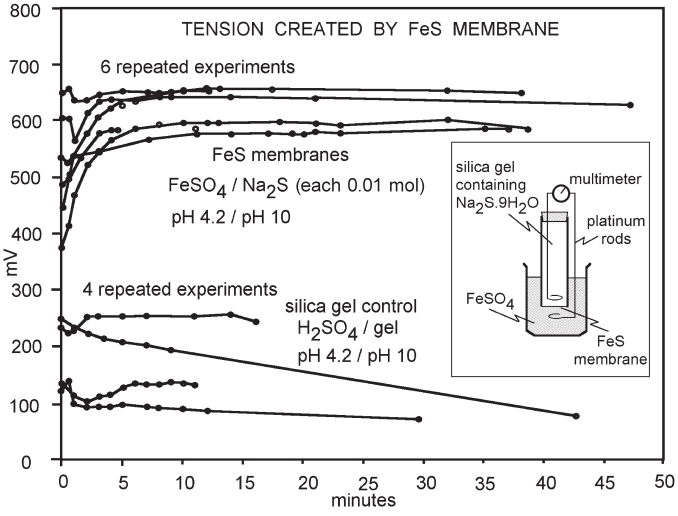

Figure 15. Plot of mV developed across an FeS membrane with time. Preliminary results with conditions as defined in the inset. Schematic illustration of the notional photoelectrochemical cell assumed to have obtained on the Hadean Earth and ocean, and of a preliminary experimental emf/pmf.

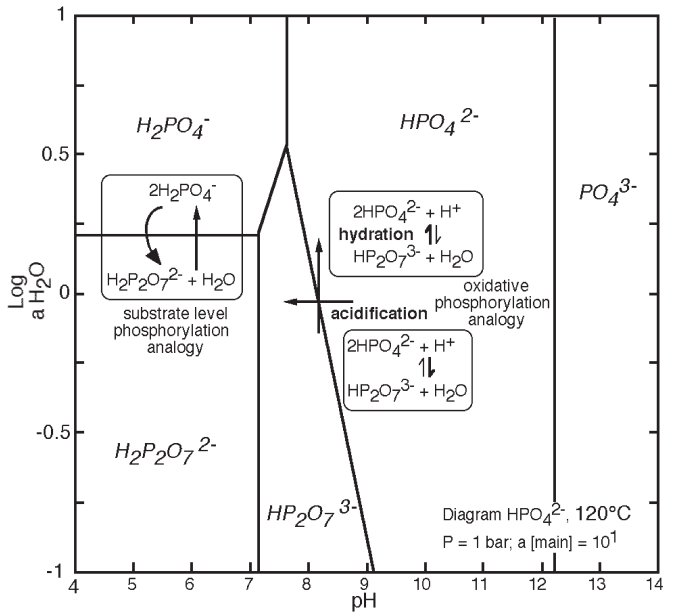

Figure 16. GWB diagram (Bethke, 1996) illustrates how *high* energy phosphoanhydride, stable at lower pH and water activity and higher T, forms from *low* energy monophosphate ($HOP_2O_6^{3-}$) and can drive dehydration polymerizations on its hydration (cf. the ATP^{4-}/ADP^{3-}/or AMP^{2-} energy cycle of life). In oxidative phosphorylation the dehydrating power of ATP is renewed by pmf (acidification), whereas in substrate level phosphorylation ATP is renewed by removal of H^+ and OH^- by a NAD-associated enzyme.

this dehydration or condensation of monophosphate (Russell and Hall, 2002):

$$H^+ + 2HPO_4^{2-} \rightarrow HP_2O_7^{3-} + H_2O \quad (15)$$

In biochemical energetics the process is known as "oxidative phosphorylation," a reference to the fact that protons are initially driven to the outside of the membrane to maintain their balance with electrons flowing outward to an electron acceptor before returning to recharge the phosphate (Mitchell, 1967) (Fig. 8). The protonmotive force is the power behind metabolism and is therefore indispensable to life, so the fact that this ambient force is a feature of the redox and alkaline-to-acid interface separated by a semiconducting inorganic membrane is a compelling aspect of the hypothesis. Nevertheless, the "ATPase" responsible for the conversion in today's organisms is a complex rotating turbo-motor (Elston et al., 1998). We assume, after Baltscheffsky et al. (1999), that the original process used a static prototype H^+-PPase, basically an enriched domain of phosphate upon mineral surfaces within the membrane (Fig. 8).

What may be surprising is the assumption that dehydrating reactions can take place in hydrothermal conditions. What to consider is the fact that anions, generated and concentrated in the membrane, would have competed successfully for a place on a growing mineral surface against the minor negative charges on the oxygens of polar water molecules. Given the centrality of acetate, the first organic phosphate may have been acetyl phosphate ($CH_3.CO.PO_4^{2-}$), perhaps produced by phosphorylation of the acetyl thioester (from equation 9) (de Duve, 1991; Russell et al., 1994):

$$CH_3COSCH_3 + HPO_4^{2-} \rightarrow CH_3SH + CH_3COPO_4^{2-} \quad (16)$$

Reacting acetyl phosphate with inorganic phosphate (HPO_4^{2-}) in the presence of Fe^{II} minerals, de Zwart et al. (2004) have generated pyrophosphate with a yield of 25% at ~40 °C. FeS was found to strongly retard hydrolysis of, and thus preserve, the pyrophosphate:

$$HPO_4^{2-} + CH_3.CO.PO_4^{2-} \rightarrow HP_2O_7^{3-} + CH_3.COO^- \quad (17)$$

The resulting pyrophosphate (PPi) would have had the energy to polymerize amino acids (Romero et al., 1991; Baltscheffsky et al., 1999):

$$^+H_3N.CH_2.COO^- + HP_2O_7^{3-} + {}^+H_3N.CH_2.COO^- \rightarrow$$
$$^+H_3N.CH_2.CO.NH.CH_2.COO^- + 2HPO_4^{2-} + H^+ \quad (18)$$

The monophosphate might then have been repolymerized with protons as shown in equation 15.

Thus, before the advent of the ribosome, random amino acid polymerization could have been driven by pyrophosphate bonded through to sulfide on the surface of mackinawite in a -Fe-S-O-P- motif as suggested by EXAFS (Pattrick, 2001, personal commun.). Such a conformation is congruent with the relationship Wolthers (2003, chapter 4, Fig. 5) finds between mackinawite and arsenate. Whatever the mechanism, these first amino acid polymers or peptides probably consisted mainly of glycine with occasional alanine, aspartate, serine, and valine (Hennet et al., 1992). The last four amino acids have particular stereochemistries; i.e., they can be right-handed (dextro) or left-handed (levo). Polymerization of a racemic mix of dextro and levo amino acids would result in a heterochiral peptide; i.e., it would have had a mixed chirality. A lack of chirality is thought to be a major problem for theorists of the emergence of life (Cairns-Smith, 1982). We show later that a lack of chirality in the first peptides, far from being a problem, was a positive advantage with regard to self-organization of the constituents of the first compartments, though we must emphasize that this unregulated polymerization of amino acids, while a necessary step, was an evolutionary dead end. However, before we examine the unregulated peptides we need to take a careful look at the structure of another key metal sulfide mineral precipitated in the reactor, viz., greigite.

GREIGITE—PRE-ENZYME AND ELECTRON DOCKING SITE

The structure of greigite tends to an inverse spinel, written notionally as $SFe^{3+}S[Fe_4^{2.75+}S_4]SNi^{2+}S$ (Fig. 9A). In fact the electrons are delocalized, so there is a certain amount of valence resonance. If further nickel is introduced, the inverse spinel verges toward the true thiospinel violarite (as $SNi^{2+}S[Fe_2^{3+}Ni_2^{3+}S_4]SNi^{2+}S$). We assume that some of the hydrogen dissolved under high pressure in the hydrothermal fluid was adsorbed on, or absorbed within, the $[Fe_4S_4]$ cube. Once there, hydrogen was split to an electron (reducing the iron) and a proton (protonating one of the four sulfides), leaving a hydrogen radical. This nascent hydrogen [H•] was highly active and might have attacked a bicarbonate ion, the ultimate electron acceptor, at a tetragonally coordinated nickel site (Fig. 9A). Because of the likely contribution of greigite ($NiFe_5S_8$) to inorganic membranes developed at alkaline submarine seepages (Russell, 1988), and its similarity to the structure of the active centers to the most ancient proteins, the ferredoxins, we have suggested that molecular constructs of the mineral were, at a later stage of emergence, incorporated by peptides as the first electron transfer agents, redox enzymes and synthases (Russell and Hall, 1997, 2002; Milner-White and Russell, 2005). They are the ready-made, modular mineral clusters (Beinert et al., 1997) that, when combined with other metals and/or organic structures, constitute components of what Baymann et al. (2003) have termed "the redox protein construction kit." The kit is partly based on the (inverse) spinel or greigite structure, which contains an $[Fe_4S_4]^{-2+}$ cage or cubane in which the electrons are delocalized and in which the iron atoms have a nominal positive charge of 2.5 and have the tendency to switch valence.

FROM CATALYSTS TO ENZYMES

We have seen that iron sulfides and iron nickel sulfides have the catalytic propensity to produce some of the simple molecular modules of life from inorganic constituents. Examples of

organic products are methane thiol, the simple amino acids, and acetate. As acetate is the likely first major product of the hydrothermal reactor or mound, it is instructive to consider how modern homoacetogens (i.e., acetogenic bacteria that use only inorganic nutrients and fuel) synthesize acetate (Müller, 2003). The overall reaction of the acetyl-coenzyme-A pathway is shown in equation 12. The key enzyme of the pathway is carbon monoxide dehydrogenase (CODH) (Peretó et al., 1999; Dobbek et al., 2001). As a single unit or homodimer, the enzyme employs five $[Fe_4S_4]$ clusters including a unique $[Fe_4NiS_5]$ cluster where CO_2 is reduced to CO (Figs. 9B, 9D). A more complex form of the enzyme possesses additional FeS clusters and reduces not only CO_2 to CO, but also condenses Ni-bound methyl and CO, yielding a Ni-bound acetyl moiety that is transferred to co-ASH in the acetyl-coenzyme-A synthase reaction (Fig. 9E) (Lindahl, 2002). The formula of the $[Fe_4NiS_5]$ C-cluster in the enzyme is also comparable to that of greigite $[Fe_5NiS_8]$ (Fig. 9C–E). Indeed, the $[Fe_4S_4]$ cube of greigite is also congruent, or nearly so, with the cubanes in the most ancient proteins, the ferredoxins (Eck and Dayhoff, 1966) (Fig. 9B). That there is some play in the placing of the Fe and Ni ions and of their charge in greigite is also echoed by the way Ni and Fe are variously but characteristically sited in the dehydrogenases (redox enzymes) and synthases (biosynthesis enzymes) (Fig. 9C–E). We have considered the component building blocks of the greigite structure to be the likely "ready-made" molecules co-opted by early life before they could be interred in sulfides or oxides (Russell and Hall, 1997; Russell and Martin, 2004; and see Bonomi et al., 1985).

THE ORGANIC TAKEOVER

Recalling our inorganic predilection, we use the way metals are coordinated in minerals and their natural cluster precursors as a heuristic device to inform us as to the likely, or at least possible, coordination chemistries adopted by early biology. Metals now constitute the active centers of ~50% of all protein types (Jernigan et al., 1994). This percentage will be optimal for the present-day geochemical environment where metals are harder to come by. Mono-, di- and tri-phosphates are also vital to coenzymes. At the onset of life amino acid polymers—the peptides—would have sequestered and protected the ubiquitous active inorganic centers in what was the first stage in an organic takeover. The peptides are the mediators of the takeover.

Amino acids are zwitterions, amphoteric molecules that have a negative and a positive charge ("zwitter" is German for hermaphrodite) as well as an organic side chain R—except for glycine ($^+H_3N.CH_2.COO^-$), which only caries a hydrogen atom. In normal conditions amino acids have a negatively charged carboxyl group ($-COO^-$) and a positively charged amino group ($-NH_3^+$) e.g., $^+H_3N.HCR.COO^-$. Before the advent of RNA, amino acids could have been polymerized by the loss of the constituents of water, OH^- from the carboxyl of one amino acid and of H^+ from the next. The reaction may have been driven by pyrophosphate hydration where water activity was low (Baltscheffsky et al., 1999) (equation 18). Alternatively, where sulfide concentrations were high, the more reactive thiocarboxyl group ($-CSO^-$) might have been attacked by the amino group with the loss of a thiol (RSH) (Wächtershäuser, 1992). There are also experimentally inspired suggestions for peptide formation (Ferris et al., 1996; Huber and Wächtershäuser, 1998; Huber et al., 2003; Leman et al., 2004), but a mechanism for prebiotic polymerization has yet to be agreed.

PEPTIDE NESTS FOR SULFIDES AND PHOSPHATE

Potentially the two structures involved in energy transfer are the metal sulfide clusters and the phosphates. The early sulfide clusters are likely to have been sequestered by thiolate (e.g., $[Fe_4S_4][CH_3S]_4^{2-}$) in aqueous solution (Bonomi et al., 1985). Thus both the phosphates (e.g., $HP_2O_7^{3-}$) and the thiolated iron(nickel) sulfide clusters were anionic. As the nitrogens of the amino groups carry a δ^+ charge even when part of a peptide, the inorganic anions would have been drawn to these δ^+ charges on the peptide chain (Fig. 17). At the same time the chain would have bowed to satisfy the negatively charged clusters. Encased in such

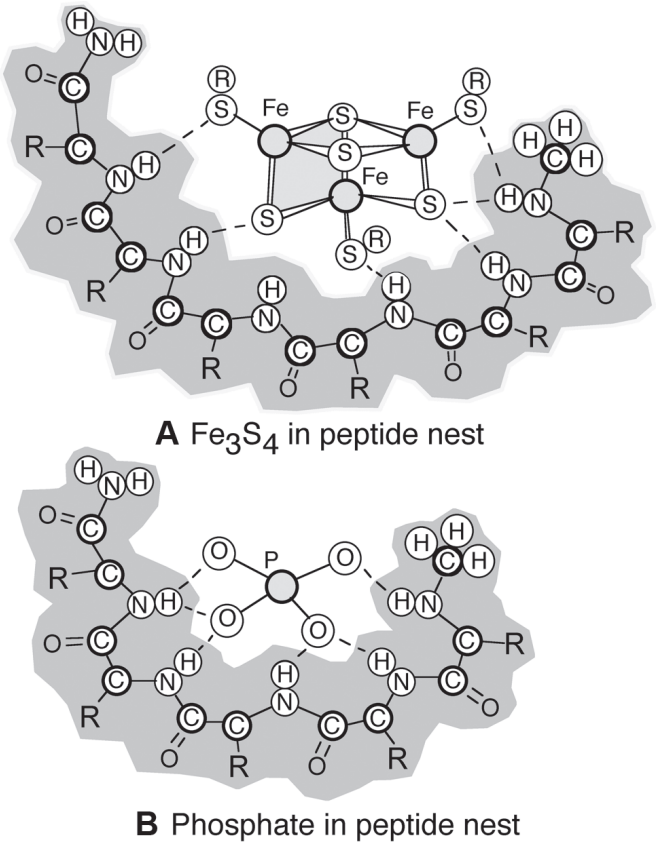

Figure 17. Ball and stick sketches of early nests of short peptides constituting alternating glycines with other abiotic racemic amino acids binding (A) an $Fe_3S_4(RS^{3-})_3$ to produce a protoferredoxin, and (B) an inorganic phosphate in a primitive P-loop. R represents side chains. After Milner-White and Russell (2005).

"peptide nests" the active centers were partially protected from dissolution, or nucleation and crystallization, and would have remained active (Milner-White and Russell, 2005). The cosseting of active centers in this way would have been optimal when the peptide was composed either of glycine, the one achiral amino acid, or of amino acids with random stereochemistries. In other words, for efficient self-organization of protoenzymes (i.e., the ferredoxins, dehydrogenases, and synthases) and the proto-coenzymes (e.g., PPi) it is better for the peptide to have been heterochiral and have consisted of racemic amino acid residues. Chiral peptides would tend to have formed helices or sheets rather than nests. The nest configuration was a likely early outcome because the easiest amino acid to make abiotically is glycine and because the other abiotic amino acids would have been racemic (Hennet et al., 1992; Huber and Wächtershäuser, 2003).

We have seen how electrons, carried first as constituents of the hydrogen molecule in hydrothermal solution, seek out electron acceptors. These are ferric iron and the more recalcitrant carbon dioxide or bicarbonate (Figs. 6D, 13, 18). Electron transfer agents and catalysts are required for the redox reactions. Later in evolution sulfate, nitrogen, and nitrate also came to be used as electron acceptors (Fig. 18). Depending on what oxidation or reduction takes place, electrons had to be transported singly, two at a time, three at a time, or even four at a time. Simple and multiple twinning to dimers and multidimers of the [4Fe-4S]-bearing ferredoxin, results of gene duplications, facilitates multiple electron flow (Adman et al., 1973; Steigerwald et al., 1990) (Fig. 19). But these complex proteins could only have formed when peptides were relatively long and had particular and regulated amino acid sequences to facilitate their folding and the sequestration of the inorganic active clusters.

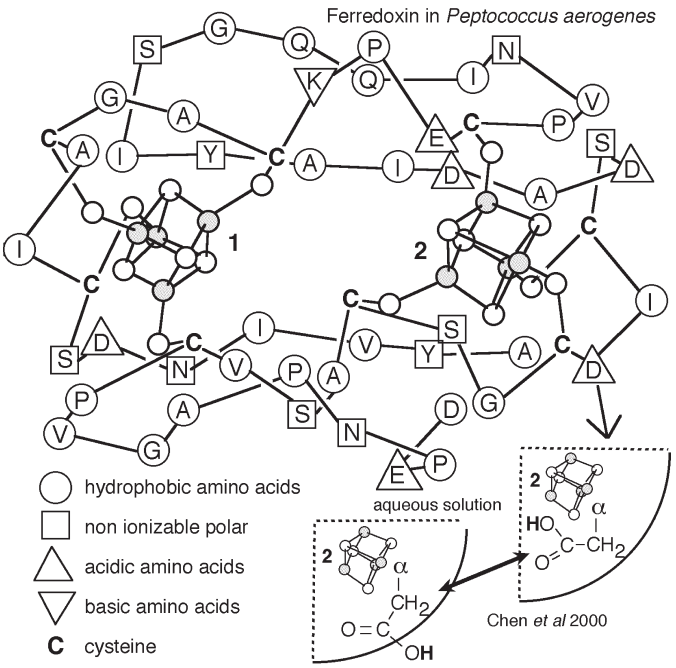

Figure 19. Ferredoxin in *Peptococcus aerogenes* as a comparison to a nested [4Fe-4S] cubane shown in Figure 17A. This is a typical ferredoxin of the type that probably formed by the twinning of a single cubane ligated through cysteines. This ferredoxin has a total of 54 simple amino acids (redrawn form Adman et al., 1973). Inset shown is the mechanism of the transfer of a solvent proton to the buried redox center via the side chain of aspartate (Chen et al., 2000). (A—alanine, Y—tyrosine, V—valine, I—isoleucine, N—asparagine, D—aspartate, S—serine, C—cysteine, G—glycine, K—lysine, P—proline, E—glutamate, Q—glutamine.)

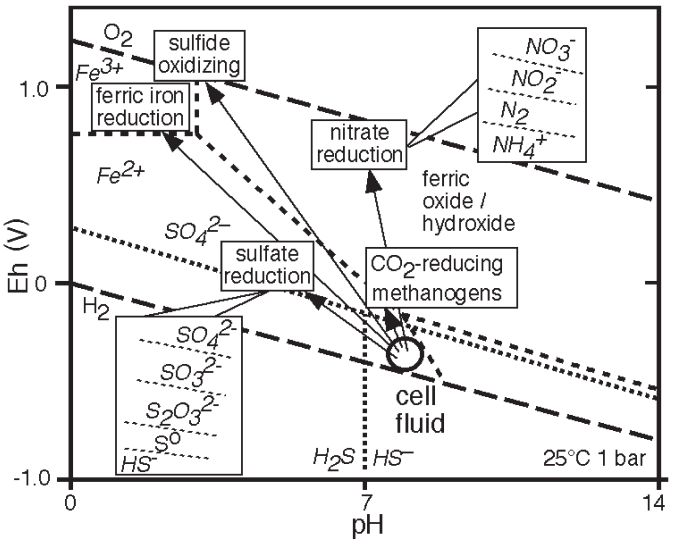

Figure 18. Redox potential/pH vectors between the cellular fluid of prokaryotes and that of the living environment represented by electron acceptors. After Russell and Hall (1997).

COENZYMES WITH ORGANIC RING COMPONENTS

One of the first requirements for organic molecules during early evolution was to cooperate with the redox tasks of the ready-made metal-bearing clusters and their associated peptides. Carbon/nitrogen rings containing three conjugated double bonds and unpaired and delocalized electrons are the coenzymes that carry out some of these processes (Pullman, 1972). Furthermore they have the advantage of being bonded to aliphatic compounds involved in structuring the cell. All the nucleic acid bases and the three aromatic amino acids have such rings as, or on, their side chains (Fig. 20). In terms of the organic takeover, the ferredoxins originally involved in the oxidation of glucose were largely replaced by nicotinamide adenine dinucleotide (NAD) (Daniel and Danson, 1995). And, when iron is in short supply, flavodoxins can substitute as electron carriers for ferredoxins.

Although the heterocyclic rings do not grow to mineral proportions, some of them polymerize to macrocyclic compounds. These compounds can sequester a variety of single metal ions coordinated through four nitrogen atoms (Eschenmoser, 1988). Different metal ions can bestow remarkably different properties

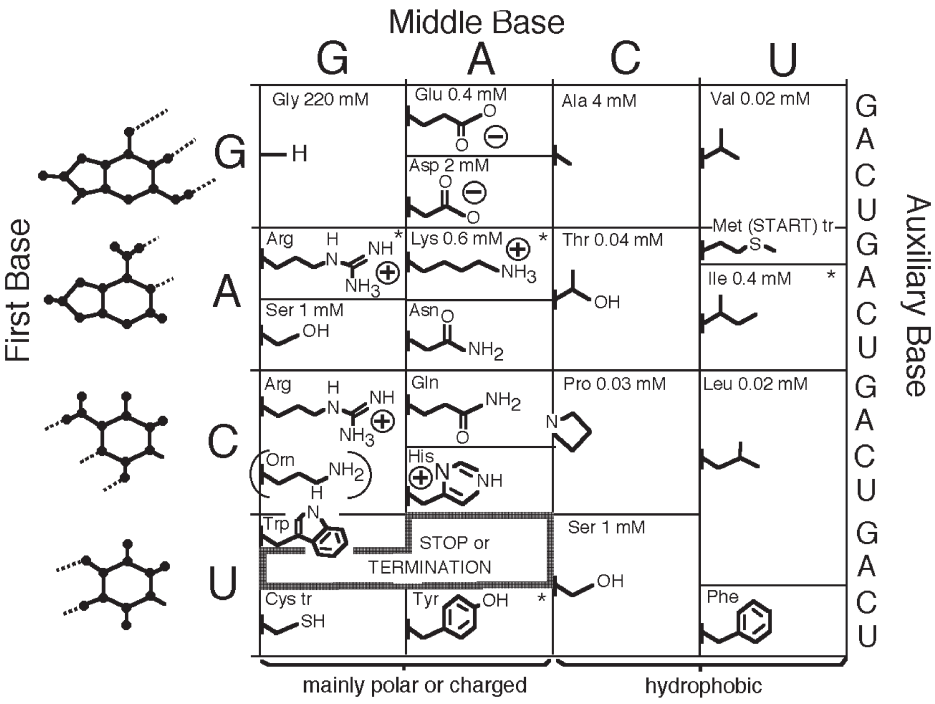

Figure 20. Table of the "universal" genetic code. Side chains of amino acids are shown to be mainly distinctive for three-letter codons, which consist of First Base, Middle Base, and Auxiliary Base. Hence, AAG and AAA are codons for lysine but the only codon for methionine is AUG (Fig. 21). Concentrations indicate amino acids that have been obtained in "prebiotic" syntheses (Hennet et al., 1992; and see Marshall, 1994) and are therefore assumed to be the commonest on the early Earth. Ornithine, not analyzed for in Hennet et al. (1992), has been tentatively assigned to the arginine codons because of the similar nature of their side chains and because arginine has not been recorded in abiotic experiments. The four starred amino acids have been shown to attach to RNA strands that contain their codons. (From Russell et al., 2003 and references therein.)

on these organometallic compounds. Cobalt and nickel corrinoids are involved in biosynthesis; magnesium (and in acid solutions, zinc) produces the chlorophylls used in photosynthesis; and iron produces the heme groups used for electron transfer and in oxygen chemistry (Eschenmoser, 1988). Pratt (1993) considers the structures based on the macrocyclic corrin ligand to date back four billion years. They certainly must be older than 3.8 Ga, for photosynthesis employs a myriad of such structural variants (Blankenship, 2002).

THE PARTICULAR PROBLEMS OF RNA SYNTHESIS

No special place in this "unintentional" world is given to RNA in our decentralized system beyond its being metabolically useful and therefore a surviving molecule. Although an unstable entity, once formed RNA would have been less mutable when secured upon a mineral surface, especially in the presence of highly reduced fluids. Nevertheless, the synthesis of nucleic acids, composed of a phosphorylated ribose sugar attached to one of four possible bases, is a problem more daunting than that of the amino and carboxylic acids. As a start we note that pyrophosphate, introduced through volcanoes to the early oceans, would have remained in solution in the relatively acidic ocean, although some would have been precipitated as vivianite ($Fe_2(PO_4)_2.8H_2O$) and as a condensed pyrophosphate on mixing with moderate-temperature alkaline fluids at the hydrothermal mound (Rouse et al., 1988; Yamagata et al., 1991; Russell and Hall, 1997; de Zwart et al., 2004). There are plausible hydrothermal sources of NH_3 and HCN to explain the synthesis of some of the bases of RNA (Schulte and Shock, 1995; Shock et al., 1998). As noted by many others, both bases and a variety of sugars can be formed at low temperature by the condensation of hydrogen cyanide and phosphoglycerate, respectively.

The carbon nitrogen ring compounds constituting some of the nucleic acid bases may have formed by the condensation of HCN on a sulfide surface such as pyrite (Leja, 1982; cf. Sowerby and Heckl, 1998). Adenine $(HCN)_5$, the most common of the bases, vital to energy storage as well as one of the components of RNA, may have formed this way (Oró and Kimball, 1961). And guanine might also have been synthesized in hydrothermal conditions, but at low yields (Ferris et al., 1978). Uracil is a hydrolysis product of HCN oligomers (Voet and Schwartz, 1982). But how or whether unstable cytosine formed at this early stage is not known.

The synthesis of ribose phosphate, the particular pentose sugar attached to the bases, is also difficult to understand but may have been the stable end product, assembled upon a mackinawite surface, from a reaction between phosphorylated chiral glyceraldehyde (GA3P) and the achiral dihydroxy acetone phosphate (DHAP), themselves derived by condensation of formaldehyde adsorbed from the alkaline fluids upon FeS (Quayle and Ferenci, 1978; Schulte and Shock 1995; Pontes-Buarques et al., 2001; Rickard et al., 2001; Russell et al., 2003; Ricardo et al., 2004). If so a feedback or autocatalytic cycle may have been initiated, with a contribution from activated hydrogen that acted as another sink for carbon dioxide (Russell et al., 2003). Phosphogluconate formed in this way decomposes exothermically to GA3P and DHAP again. Reaction between the ribose phosphate adhering to the mackinawite surface and the bases would then produce RNA.

Of course it may be that the particular nucleic acids used before life had fully developed were different, and/or that there were two rather than four bases (e.g., Reader and Joyce, 2002), perhaps adenine and uracil (Jimenez-Sanchez, 1995). We are forced to step over this period for lack of knowledge. Anyway, apart from the easily synthesized adenine, only small concentrations of the rest were needed because, as we shall see, RNA polymers were the "molds" that may have produced a myriad of peptide "casts."

THE ORIGIN OF THE CODE AND THE FIRST CODED POLYMERS OF PARTICULAR CHIRALITY

Although the analogue of the acetyl-coenzyme-A pathway provides a sink for carbon dioxide in the early atmosphere and ocean, and it is possible to envisage how such a growing system would bud and reproduce, this is insufficient for replication and evolution. For this a code was required, probably reliant on a replicating and evolving RNA, to generate and order functionally useful peptides. In living cells amino acids are sequenced and polymerized in a process centered on the ribosome, composed essentially of RNA, that ratchets along messenger RNA (Ban et al., 2000). Such a complex process must have evolved from a simpler system. A hint of what this was is provided by the shape of the RNA codons and the characteristics of the amino acid side chains (Fig. 21).

Geologists are less familiar with the structures of the carbon-, nitrogen-, and oxygen-bearing main-chain polymers and their various and characteristic side chains that constitute the amino and nucleic acids than they are with the internal structure of minerals. Nevertheless, the way the side chains of the organic polymers might have been packed together on a mineral surface, if only ephemerally, takes some of the mystery out of how life works or worked—how, for example, nucleic acid polymers may have first adventitiously coded for peptides and proteins. Looking at the origin of the code from a mineralogical perspective leads us to follow Woese (1967) in his view that genetic information was first transferred directly by selection through a somewhat indiscriminate "codon-amino acid pairing," which relied upon the affinity of the shape and charge of the codon (a triplet of three nucleic acids) to the shape and charge of the amino acid and especially of its side chain (Woese et al., 1966: Woese, 1967, p. 174–175). Thus, what is known as the peptidyl transferase reaction of an RNA molecule probably evolved via direct translation on a protoribosome (Woese, 1967). This relationship happened to provide a rudimentary but direct coding to the polymerizing amino acid sequence.

Developing this idea, Mellersh (1993) emphasized that RNA triplets would only offer a cleftlike (tridentate) conformation to attract amino acids when adhering to a solid phase. For such a solid phase we favor mackinawite (Russell et al., 2003). We have already noted that phosphates may coat a mackinawite surface and there act as a random polymerizing agent for peptide formation. The phosphates of RNA also could have been bonded through to sulfide on the surface of mackinawite in the same way (Fig. 21). First and foremost we should see the affinity between the RNA triplets as offering a mechanism of polymerization more efficient than the chance condensation of amino acids on a simple phosphorylated mineral surface. The rows of RNA triplets could have gripped and juxtaposed amino acid monomers in such a way as to offer the carboxyl group of one to the amino group of the next for

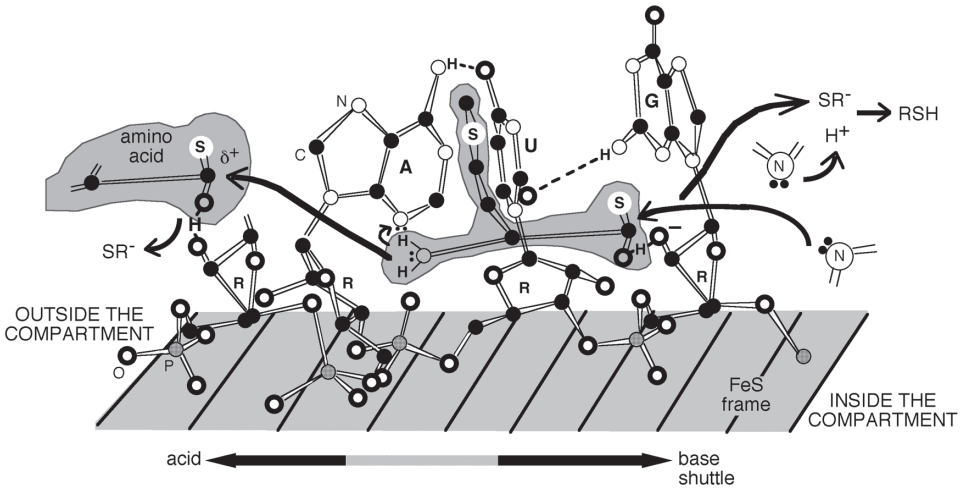

Figure 21. Sketch to show how an amino acid may have been gripped by an RNA triplet (AUG) and offered its nucleophilic amino group to the electrophilic carbon of the thiocarboxyl group of an adjacent amino acid to dimerize (Mellersh, 1993; cf. Muth et al., 2000, fig. 2). A nitrogen atom acts as the basic binding site for the amino group on adenine (A), and oxygen on the next ribose (R) acts as the binding site of the matching thiocarboxyl group. A peptide chain built incrementally in this way would be released by acid-base catalysis (Muth et al., 2000). There would have been a tendency for the AUG triplet to act as the codon for methionine as shown here, if available in the FeS membrane (Mellersh, 1993; Russell et al., 2003). If not, another hydrophobic amino acid at relatively high concentration was likely to have occupied the site.

bonding (Mellersh, 1993). At the same time the affinity between the clefts of RNA and the side chains of the amino acids would happen to effect crude selection by codon-amino acid pairing as envisaged by Woese (1967). For example, clefts in which uracil was the central base would tend to attract only amino acids with hydrophobic side chains such as that of methionine (NH_3^+.CH_2.$(CH_2)_2$.SH.CH_3.CSO^-), whereas those in which adenine was central would show affinity for the hydrophilic charged or polar amino acids (Figs. 20, 21).

We assume amino and nucleic acids would have occupied the iron sulfide cells, though the former would have vastly outweighed the latter, and the crude coding of, or translation to, peptides would have been a feed-forward process. RNAs on the surface of nanocrystals may themselves have replicated, where water activity was low, by Watson-Crick hydrogen bonding in which A bonded to U and G bonded to C (Béland and Allen, 1994). The "protoribosome" would then have operated as a replicase, via the replication of triplets (the "triplicase" of Poole et al., 1999). The first cycle of replication provided an antisense codon, so that a GCC triplet (the codon for alanine and the most likely first triplet) produced the antisense codon "read" in the opposite direction as GGC (glycine) (Trifonov, 2000). Therefore, as touched on above, if the initial triplet coded for a hydrophilic amino acid (with adenine occupying the central position), then its opposite would have coded for a hydrophobic residue (with uracil as the central base) (Béland and Allen, 1994; Konecny et al., 1995).

Point (single base) mutations on these triplets would have tended to code for the amino acids synthesized by Hennet at al. (1991), i.e., glycine (GGC), alanine (GCC), aspartate (GAC), and serine (UCC). More astonishing is the fact that these amino acids constitute the common sequence in that group of metalloproteins acknowledged to have the longest pedigree, the ferredoxins (Eck and Dayhoff, 1966; Trifonov et al., 2001; Russell et al., 2003). This system of direct coding would have been relatively robust, in that mutations not involving the central RNA monomer would have attracted amino acids with similar side chains and thereby similar properties.

However, during the organic takeover the protoribosome would have required another surface in place of mackinawite. This might have been supplied by a peptide sequence rich in positively charged side chains. Such a peptide would have attracted the phosphates of RNA that they might polymerize and still offer the triplet clefts. Lysine, arginine, and ornithine would have been equally useful in such a peptide (Fig. 20). Mellersh and Wilkinson (2000) have demonstrated that poly-adenosine, which includes the clefts AAA expected to have affinity for lysine, does stereoselectively bind L-lysine from dilute aqueous solution of L-amino acids (Mellersh and Wilkinson 2000). Moreover, about half the amount of L-arginine and L-ornithine also was found to bind with poly-adenosine. As adenosine was likely the most common of the nucleic acids, and lysine and probably ornithine can be made abiotically, then we have the makings of a feedback cycle that involves the transfer of information.

The chance stereochemistry of the short RNA polymer would determine whether it catalyzed the polymerization of D- or L-amino acids into peptides (Mellersh, 1993). To achieve a low-energy state, as with mineral growth, we might expect RNA to tend to lengthen while preserving either left or right chiralities, i.e., a favorable packing arrangement (Joyce et al., 1984). Were a monomer with the opposite stereochemistry to be added to a growing chain, growth would be thwarted (Sandars, 2003). That filter would have been sufficient to tip the holochirality scale because, despite the presence of a racemic mixture of amino acids in the microcavities, only amino acids of the same α-carbon configuration (similar stereochemistry) would preferentially have ended up in peptides, to yield a population of distinctly handed peptides. Some of these peptides would eventually feed back in a hypercyclic manner to favor the syntheses of their "stereochemically appropriate" polymerizing template.

Eventually the more robust but less reactive DNA (deoxyribonucleic acid) molecules took over from RNA and thence survived. Braun and Libchaber (2004) have demonstrated that secondary convection and thermophoresis driven by temperature gradients within microcavities in a hydrothermal mound could have concentrated, elongated, and driven the replication of DNA. It remains to be seen if RNA could be elongated and replicated by the same process.

Although the codon-amino acid affinity concept explains why the chiralities of polynucleotides and peptides in life are opposite, a relationship not required by Crick's (1968) frozen accident hypothesis, it does not explain why, on our planet, dextro-DNA and RNA code for levo-proteins. As the energetic differences between right- and left-handed chiral molecules, even for thiosubstituted DNA analogues, are negligible (MacDermott et al., 1992) and would have been "lost in the noise" within a natural hydrothermal reactor, we can only conclude that both chiral forms emerged separately, but that at some unknown stage the present pairing survived, either by fortuitously stealing a march on the other, perhaps through the chance development of a better ribosome, or later in a chirality war between the rival prokaryotes within the biosphere.

A HYDROPHOBIC ORGANIC MEMBRANE

As abiotic lipids of equal carbon chain lengths are unlikely to have been delivered to, and survived on, early Earth in quantities large enough to have allowed continued reproduction (Cairns-Smith, 1982), we have been left to consider FeS bounded "cells" as the hatcheries of life. Short noncoded peptides generated in hydrothermal conditions (Russell et al., 1994; Huber and Wächtershäuser, 1998, 2003; Ferris et al., 1996) could have played an important role in improving membrane characteristics. These peptides and other polymers produced in the mound would have coated the inside of inorganic compartments and partially plugged pore spaces. Excess organic sulfides and nitrides also could have been "entropy driven" into this, the first organic membrane (Cole et al., 1994). We imagine these polymers to

have cohered to form proteinaceous membranes and walls to protocells—organic structures that offered several advantages. Eventually, genetically controlled proteinaceous cell envelopes composed substantially of hydrophobic heterochiral peptides, for example, would have the advantage of including metal clusters such as the $[Fe_4S_4]$ centers within their structure as stabilizers and electron transfer agents. At a later stage lipids would have been generated from acetyl-coenzyme-A by continued addition of C_2 components, perhaps until the stable C_{12} fatty acid (dodecanoate) was realized (Fig. 12) (Shock et al., 1998). Once this happened, lipids would have more efficiently denied protons an uncontrolled short circuit back into the cellular interiors.

EARLY EVOLUTION AND THE COMMON ANCESTRAL COMMUNITY

The universal ancestor of life probably comprised a community of single-celled organisms still housed within its hydrothermal hatchery that possessed all of the attributes common to all Bacteria and Archaea: the genetic code; the ribosome; DNA; a supporting core and intermediate metabolism needed to supply the constituents of its reproduction; replication; compartmentation from the environment; redox chemistry; and the use of a proton gradient. This last common community (the LCC of Woese, 1998; Macalady and Banfield, 2003) existed in the hydrothermal mound at the dawn of the biochemical revolution where genes and proteins were diversifying into a myriad of functions, where metal sulfide catalysts were being replaced by proteins, where new pathways and cofactors were being invented to augment and substitute their mineral and RNA precursors, where FeS was being incorporated into proteins as Fe(Ni)S clusters, an imprint of which would be reflected in the FeS centers of ancient protein, and where biochemistry started to diversify into the forms that were both possible and useful (Eck and Dayhoff, 1966; Hall et al., 1971; Martin and Russell, 2003) (Figs. 14, 19).

From the standpoint of protein structure, this age of invention would have witnessed the origin of basic building blocks of biochemical function that (i) are conserved at the level of 3D structure among Bacteria and Archaea and (ii) are recognizable as functional modules in various electron transporting proteins (Beinert et al., 1997; Baymann et al., 2003). From the standpoint of amino acid sequence complexification, this age of invention would have been a phase of molecular evolution where proteins were diversifying and improving their efficiency (Baymann et al., 2003).

It has been argued that the first acetogens were the forerunners of the Bacteria (Fig. 14) (Russell and Martin, 2004). We suggest that a minority of these cells, derived from those that emerged at around 40 °C, exploited the potential offered at higher temperature deeper in the mound where the kinetic energy was greater and the activation energy required for reduction, through acetate (equation 8), all the way to methane (equation 7), was lower. These first so-called methanogens may have evolved while still in the mound, as there is even more energy to be had in the full reduction of carbon dioxide (Amend and Shock, 2001). Moreover, the catalytic/enzymatic machinery required is similar (Thauer, 1998; Fontecilla-Camps and Ragsdale, 1999).

Before their release from the mound the first cells would have responded to environmental differences deterministically in a manner more comparable to an ecosystem than to an individuated cell. Compartments near the edge of the hydrothermal mound, those most distant from the "inorganic formative fluid" (cf. Haeckel, 1892), lie in the steepest chemical, electrochemical, and thermal gradients but at lower temperature. It is here that H^+, FeOOH, PPi, and CO_2 were most concentrated, and this was where we assume the onset of life to have taken place at around 40 °C (Fig. 14). At this early stage, mineral circumscribed compartments in the more restricted environment below this distal group and closer to the hydrothermal fluid were hotter, and though the gradients would have been lower and the immediate environment would have been more depleted in the constituents mentioned above, concentrations of CO, H_2, thiols, and the abiotic amino acids would have been higher. In this proximal zone elemental sulfur polymers, generated in the atmosphere by photolysis of H_2S and SO_2 (Pavlov and Kasting, 2002) and sedimented within the mounds, could stand in as an electron acceptor in place of ferric iron, albeit at a lower potential (Fig. 6D) (Stetter and Gaag, 1983). Alternatively, if cells deeper in the mound were beyond the reach of external electron acceptors, another way of ridding the system of excess reductant was through the discharging of electrons to the oceanic and atmospheric sink in CH_4 (de Duve, 1991).

Evolution in the mound extended beyond mere optimization of the acetate and methane reactions (Martin and Russell, 2003). A next step was adaptation that exploited the reduced carbon and energy to be found in waste products and dead cells:

$$CH_3.COO^- + 8Fe^{III} + 4H_2O \rightarrow 8Fe^{2+} + 2HCO_3^- + 9H^+ \quad (19)$$

The prior use of Fe^{III} as an electron acceptor during autotrophic biosynthesis (equation 14) provided a means of such respiration (oxidative metabolism) (Vargas et al., 1998). Other potential electron acceptors were photolytic S^0 and Mn^{IV} (Figs. 6D, 18) (Nealson and Stahl, 1997; Bahcall et al., 2001; Baymann et al., 2003).

We conclude that the last common ancestral community occupied the very hydrothermal hatchery in which life first emerged. The proto-Bacteria were initially suited to low to moderate temperatures, and the proto-Archaea originally evolved to withstand the shock of relatively high temperatures (i.e., ~60 °C) (Fig. 14). 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 a meteorite impact or by a carbon dioxide greenhouse (Kasting and Ackerman, 1986; Kasting and Brown, 1998; Nisbet and Sleep, 2001) could explain why the last common community may have been thermophilic, perhaps living at 50–60 °C (Gaucher et al., 2003 but see Brochier and Philippe, 2002).

DIFFERENTIATION INTO TWO DOMAINS

Although the thermodynamic drives would be lower in proximal compartments of the mound (Schoonen et al., 1999), the lower kinetic barriers to reductions and condensations at these higher temperatures would encourage reaction. In these hotter compartments at first there would have been no RNA regulation of peptides, and no replication or evolution. This is because RNA is unstable at high temperature (Poole et al., 1999). But early biochemical evolution in the outermost compartments could have produced some "thermotolerant" DNA from RNA that could have invaded the metabolic husks of those below and co-opted this poorer, "thermochallenging" environment (Fig. 22) (Forterre, 1995, 2002). Glansdorf has argued that cotranslation of functionally related proteins from integrated anabolic genes "facilitated the formation of multienzyme complexes" that channeled thermolabile substrates that could invade hotter environments (Glansdorff, 1999, p. 432). Here inherently thermolabile proteins acted to stabilize and protect the whole ensemble (Forterre, 1995). Operons—linear sequences of genes transcribable as a single unit together with a regulatory operator—emerged as a response to these increasing temperatures (Glansdorff, 1999). Such operons would have facilitated the production of multienzyme complexes capable of reducing the deleterious effects of toxic intermediates produced by thermodegradation at high temperature. Srere (1987) points out that the clustering of the functionally related genes responsible for these complexes would also have conferred evolutionary advantage when returned to mesothermal conditions.

Let us recall the importance of a regulated dynamic system. We could show that the hydrothermal system was both thermostat and chemostat. This took the onus off the living system to be a thermostat but it would have needed its own control system for governing the internal state of the protocells. Such a regulatory power is known as homeostasis. It probably emerged as newly generated protons, driven out of the cell by electron transfer, kept the cell neutral to alkaline. This process was augmented by the oxidative formation of disulfides such as the amino acid dimer cystine, from the monomer cysteine, by protons (Russell et al., 1994):

$$2RS^- + 2H^+ \Leftrightarrow H_2 + RSSR \qquad (20)$$

At the point of differentiation or bifurcation into the two prokaryotic domains, we see the precursors to the Bacteria occupying the broad front of the growing hydrothermal mound at its interface with the ocean. The precursors to the Archaea, the sturdy but slowly evolving second domain of the prokaryotes,

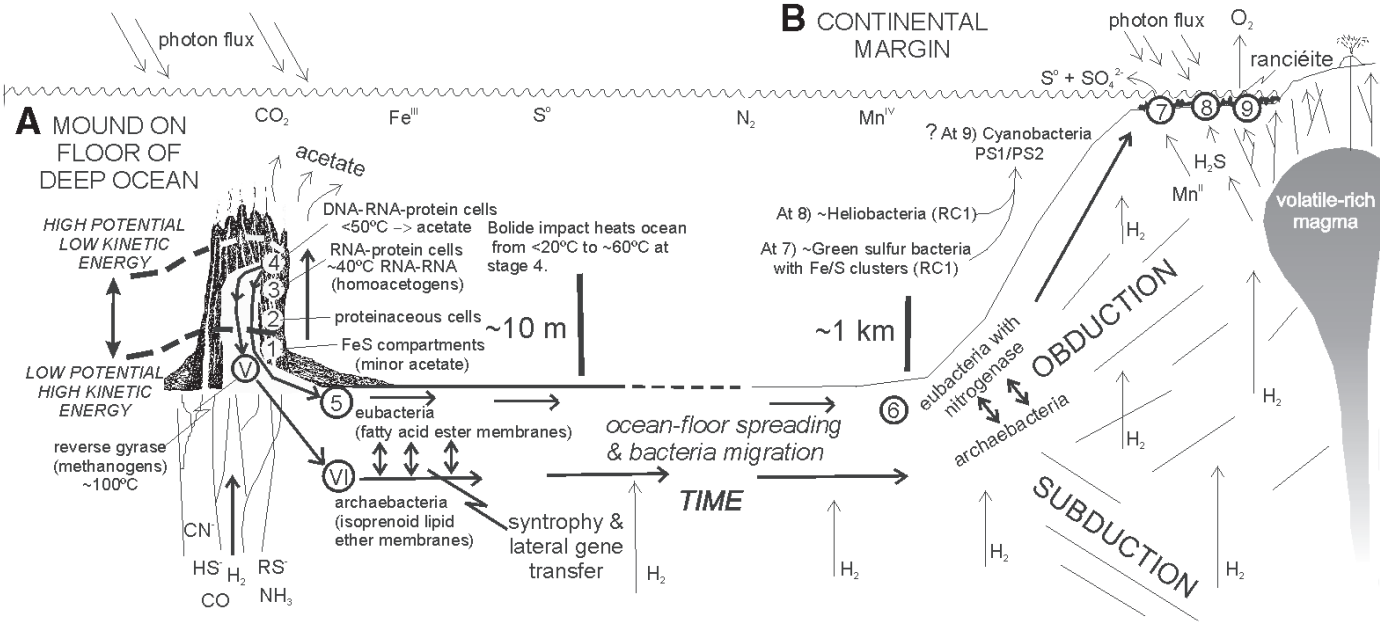

Figure 22. Chemosynthetic life emerges at a warm alkaline seepage and at (A) differentiates into the precursors of the Bacteria and Archaea, and expands downward into the surrounding sediments and crust (Martin and Russell, 2003; Russell and Martin, 2004). From here a proportion is conveyed by ocean floor spreading toward a constructive margin (B) produced by 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 (Westall et al., 2001). Oxygenic photosynthesis (9) is a further development that may have evolved at a manganiferous hot spring by 3.75 Ga. (Various scales.) (From Russell and Arndt, 2005.)

bring up the rear (Figs. 14, 22) (Woese et al., 1990; Russell and Hall, 2002). Both the proto-Bacteria and the proto-Archaea lived up to the opposite edges of reproductive viability, the former at a distance from fuel and challenged by kinetics at low temperature, the latter subject to the dangers of pyrolysis. Certainly the Archaea appear to be the conservative cousins of the Bacteria, as though they have had to hoard resources internally and defend themselves against untoward perturbations. In the anaerobic environment that obtained in the mound at the dawn of life, some of the proto-Archaea probably lived off redox reactions that Bacteria have never mastered, relying on organic sulfides in a series of electron donations and generating methane waste (an electron carrier) from carbon dioxide without a metallic electron acceptor (Schäfer et al., 1999; Amend and Shock, 2001).

Even then, the proto-Bacteria and the proto-Archaea found it advantageous to live syntrophically both within and across domains. Cells would have interacted with their neighbors by swapping genes, providing some of the nutrients, and removing some of the waste. Unfortunates that were entrained within the hydrothermal solution and dispersed to the relative desert of the uncertain ocean could not have survived such vicissitudes and dilution of nutrient (e.g., Bjerrum and Canfield, 2002). The only safe migration route was down onto the ocean floor and into the warm sediments and permeable basalts below, where the essentials—H_2 and CO_2—were assured.

Thus we conclude that 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), although up till this time of divergence, genes were shared in what may be called a cellular cooperative (Fig. 14). This differentiation of the precursors of the Archaea from those of the Bacteria was expedited by entropy and the random changes in genes it caused. It eventually produced the two mutually exclusive genotypes (Wicken, 1987).

ESTABLISHMENT OF THE DEEP BIOSPHERE

As the proto-Archaea and the proto-Bacteria began to colonize their surrounds, they eventually found themselves expanding into the sediments and volcanic horizons at the base of the mound (Fig. 22). Here conditions were not so different excepting the much lower flux of nutrient and fuel (Wolin, 1982). Thus the deep biosphere was inaugurated (Parkes et al., 1990, 1994; Pedersen 1993). Once in the deep biosphere SO_4^{2-} and N_2 are likely to have joined Fe^{III}, S^0, and Mn^{IV} as electron acceptors (Fig. 18). Although this probably happened quickly (Pinti, 2002; Shen and Buick, 2004; Raymond et al., 2004) the age of these innovations is not known. We take the view that once chemical energy potentials are available then their exploitation is relatively rapid. Yet at these early stages mineral-like clusters would again have played a critical role in evolution. The metal center responsible for N_2 reduction is comparable to a greigite twin along the sulfur plane. excepting the presence of one proximal Mo atom comparable to a naturally occurring $MoFe_3S_4$ cluster produced from aqueous MoS_4^{2-} and FeS (Russell et al., 1994; Helz et al., 1996). This "Siamese-like twin" possibly contains a nitrogen atom in the central site (X in Fig. 9F) (Einsle et al., 2002; Smith, 2002). Exactly where and how nitrogen is reduced to ammonia via the nitride N^{3-} on this metal sulfide center is as yet unresolved (Seefeldt et al., 2004).

OBDUCTION AND PHOTOSYNTHESIS

We have noted that conditions for the earliest cells in the open sea were inhospitable and periodically impossible. How then do we explain the emergence of photosynthetic organisms in the full glare of hard UV from the young sun (Canuto et al., 1982)? The first step was for organisms to have approached the photic zone with the "safety of numbers." Because of the particular geometry of Hadean oceanic crust, buoyant sediment and hydrated basaltic crust piled up over the subducting, delaminated, eclogitized lower parts of the slab (Russell and Arndt, 2005). There were no deep ocean trenches. Obduction and uplift of oceanic sediments, and of the hydrated basalt beneath, passively transported some bacterial colonies into shallow water and into the photic zone on the margins of volcanic chains (cf. Margolis et al., 1978) (Fig. 22). Cells were protected from deleterious solar radiation beneath a mineral coating (Cockell and Knowland, 1999). Opportunistic protection by superposed minerals and mineral excretions are well-known survival gambits (Phoenix et al., 2001). In these conditions some Bacteria near the surface augmented their protective shield 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, Zn, Co, and Ni could have been sequestered in variants of what is known as the corrin ring, itself comprising four C/N rings (Eschenmoser, 1988). Pigments developed for photoprotection could then have been adapted as electron transfer agents, as photosynthetic reaction centers and antenna proteins (Fig. 2B) (Mulkidjanian and Junge, 1997; Allen, 2004).

Sediments in and overlying an obducted pile are likely, in places, to have been subjected to hydrothermal H_2S of magmatic or metasomatic derivation (Fig. 22). The first photosynthesist may have been a precursor of the green sulfur bacteria. As the name suggests, like many "primitive" bacteria, they relied on hydrogen sulfide as an electron donor (Baymann et al., 2001; Blankenship, 2002). In these conditions, a reaction center (RC1) was developed that could generate elemental sulfur as waste, and gain electrons for biosynthesis in the process:

$$H_2S + CO_2 + \text{light} \rightarrow (CH_2O)_{life} + H_2O + 2S^0 \qquad (21)$$

As we might expect of relatively gradualistic evolution, the green sulfur bacteria retain a reliance on iron sulfide clusters as electron transfer agents (Vermaas, 1994; Blankenship, 2002). An evolutionary variant of the fermenting bacteria, a photosynthetic precursor of the heliobacteria, could fix carbon dioxide by the concomitant oxidation of organic waste and detritus. At the

same time they used a similar reaction center (RC1) (Baymann et al., 2001; Blankenship, 2002). These two reaction centers hybridized to form what is known as photosystem 2 (PS2), the photosystem invariably employed by all cyanobacteria and the chloroplasts derived from them in plants (Michel and Deisenhofer, 1988; Allen, 2005). PS2 works in conjunction with the first reaction center (RC1), which evolved into photosystem 1 (Baymann et al., 2001). Photosystem 2 is capable, in conjunction with photosystem 1, of oxidizing two molecules of H_2O (cf. H_2S in the green sulfur bacteria and $(CH_2O)_x$ in the halobacteria) for the generation of every one molecule of O_2, while gaining four electrons and four protons for the fixation of carbon from CO_2 for biosynthesis in the process (Hansson and Wydrzynski, 1990; Allen, 2005):

$$2H_2O + \text{light} + PS2_{oxidized} \rightarrow 4H^+ + 4e^- + PS2_{excited} + O_2 \quad (22)$$

To generalize:

$$H_2O + CO_2 + \text{light} \rightarrow (CH_2O)_{life} + O_2 \quad (23)$$

Reaction 22 invariably involves the oxygen evolving center (OEC) in PS2. The OEC is a $[CaMn_4]$-structure consisting of a trigonal pyramid with calcium at the apex, 3.4Å from each of the three manganese atoms at its base: a distal manganese lies in the same plane as the other three and 3.3Å from its nearest neighbor (Loll et al., 2005). One of the manganese atoms constituting the base of the pyramid is also 3.3Å from another, whereas the other two are 2.7Å apart. To explain such an extraordinary innovation Russell and Hall (2001, 2002) assumed that anoxygenic photosynthesizers in subaerial hot spring carbonate pools adsorbed exhalative manganese precipitates onto their membranes, perhaps while using photolytic Mn^{IV} as an electron acceptor (Fig. 2C) (Burns and Burns, 1979; Myers and Nealson, 1988; Chafetz et al., 1998). In reduced form a manganese coating could protect the cells from hard UV injury (cf. Daly et al., 2004). Photo-oxidation would generate ranciéite (the calcium-bearing birnessite, $CaMn_4O_9.3H_2O$) (Anbar and Holland, 1992; Russell and Hall, 2001; 2002, fig. 6). Thus, a cluster of ranciéite may have contributed the "ready-made" $[CaMn_4]$ structure that was co-opted by one of the reaction centers, though if so the Mn-Mn distances of 2.9Å characteristic of the cluster constrained in ranciéite must have been modified to a conformation more typical of hollandite where two Mn-Mn distances are 2.7Å and two are 3.3Å (Sauer and Yachandra, 2004; Loll et al., 2005). The manganese cluster, once sequestered in this reaction center and stabilized by the calcium atom, could have oxidized two water molecules, passing four protons and four electrons from the hydrogen to the cell for biosynthesis while the oxygen went to waste (Fig. 23) (Russell and Hall, 2001). Without the calcium atom the structure would be irreversibly reduced to the cubane moiety of the spinel hausmannite (Russell and Hall, 2002, fig. 6). As it is the structure readily reverts to the oxidized form. Thus we conclude that a minimum of genetic control was required for a hydrated $[CaMn_4]$ complex

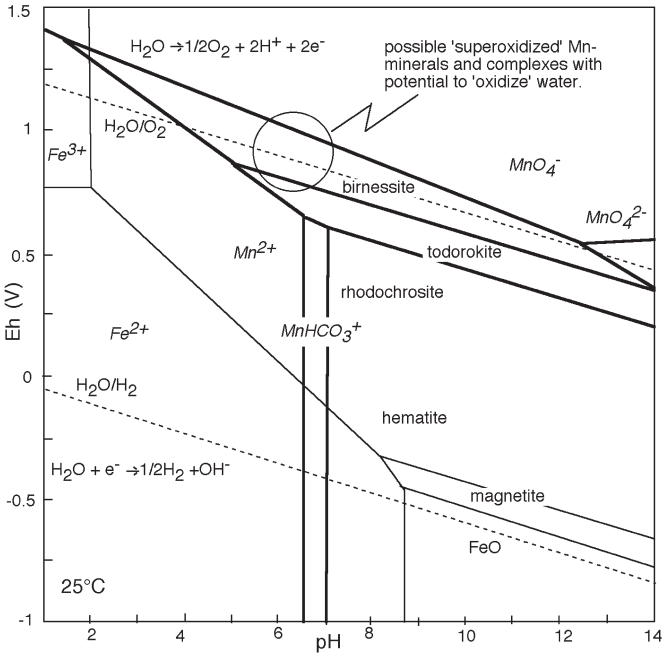

Figure 23. Mn and Fe plots (GWB) of species and phases in similar conditions. Activities of Mn^{2+} and $Fe^{2+} = 10^{-6}$; fugacity of $CO_2 = 1$ (~3000 times the present atmosphere). Pyrolusite is suppressed to favor hydrated and mixed valence oxides and hydroxides such as birnessite $[(Na,K,Ca)(Mg,Mn)Mn_6O_{14}.5H_2O)]$ and the thermodynamically uncharacterized ranciéite $[CaMn_4O_9.3H_2O]$. In theory, clusters of birnessite and ranciéite have the potential to oxidize water to the peroxide at low pH.

to take up a shape within the membrane that would have facilitated the oxidation of water (Figs. 2D, 23, 24). Invagination and evolution of the protein led to the emergence of the cyanobacteria, organisms that were eventually to change the face of the planet to its present blue-green cast (Dismukes et al., 2001).

Unless one considers the Banded Iron Formations to be a good indicator (Holm, 1987; Dymek and Klein, 1988), the impact of oxygenic photosynthesis is not discernable until the early Proterozoic (Bekker et al., 2004). However, Rosing (1999) and Rosing and Frei (2004), remarking on the apparently high rates of organic production, advance morphological, as well as stable and radiogenic isotopic evidence, to favor an origin of oxygenic photosynthesis prior to 3.7 Ga. And there is independent sulfur isotope evidence for the presence of trace atmospheric oxygen by 3.5 Ga (Ohmoto et al., 1993; Shen and Buick, 2004). Because we can see no reason why, given the appropriate conditions, the emergence of oxygenic photosynthesists from anoxygenic photosynthetic bacteria should have taken any longer than the emergence of life, these inferences, surprising to some (e.g., Blank, 2004), seem entirely reasonable. The long lag time between the photobacterial production of oxygen waste and its appearance as an atmospheric gas in the early Proterozoic (Farquhar et al., 2000) must then be explained by the reductive capacity of the planet, particularly of reduced iron, organic detritus, and biogenic

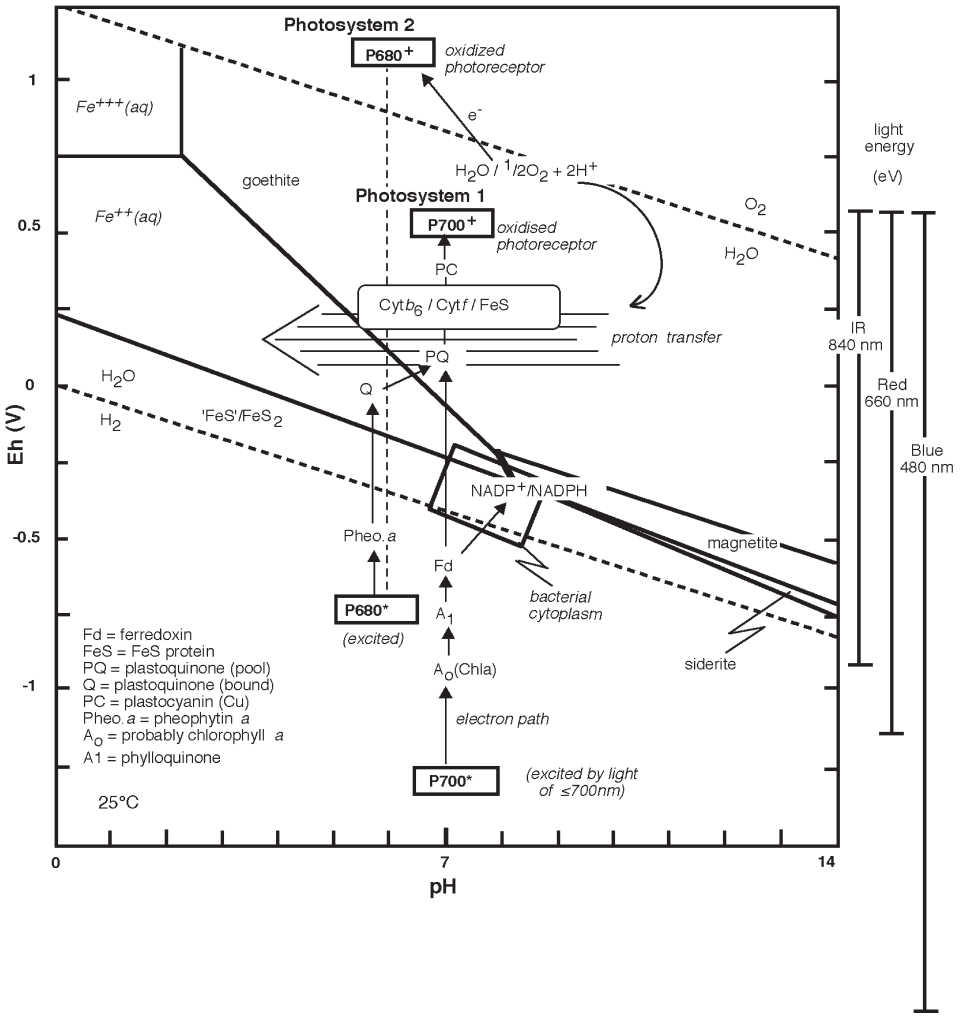

Figure 24. Electron pathways of oxygenic photosynthesis for cyanobacteria for pH = 7 though photosystem 2 (PS2) is displaced for clarity. In non-cyclic photophosphorylation $NADP^+$ is reduced by electrons from PS1 to make NADPH; PS2 provides an electron to replenish PS1 whereas dissociation of water to evolve oxygen provides the electron to replenish PS2. In cyclic photophosphorylation only PS1 is used and $NADP^+$ does not receive an electron; protons are transferred out of the cell, generating a pmf that produces ATP. Photosynthetic production of NADPH, ATP and protons contribute to the synthesis of carbohydrate from CO_2. Light provides an alternative source of redox energy for H_2 provision of chemical energy (Fig. 2) although FeS remains at the core of the energy-transfer system (cf. Blankenship, 2002, Figure 11.7).

methane (Lécuyer and Ricard, 1999; Kasting, 2001; Catling et al., 2001; Bjerrum and Canfield, 2002; Bekker et al., 2004).

CONCLUSIONS

The onset of life was not a haphazard affair but the metastable evolutionary outcome of focused reactions between hydrothermal hydrogen and bicarbonate in the ocean, with inputs from trace metals, phosphate, and ammonia. Considering the fragility of some organic polymers, especially RNA, and the theoretical and experimental support for pyrophosphate and organic synthesis at moderate temperatures, ~40 °C is a likely temperature for life's emergence (Moulton et al., 2000). Life would have emerged as soon as such a temperature was realized—a state probably reached, at least intermittently, by 4.3 Ga (Nisbet and Sleep, 2001). Convection cells operating within the oceanic crust in the relative tranquility of ridge flanks or in the deep ocean floor would have produced hydrothermal mounds—mounds that also would have acted as chemical fractionation reactors. The free energy of reaction between H_2 and CO_2 increases with decreasing temperature though the kinetics become ever more sluggish (Shock, 1992). The main products of the reaction are likely to have been acetate and water (Huber and Wächtershäuser, 1997). Other products such as glycine (amino acetate), other amino acids, and traces of nucleic acids constituted the first organic molecules (Russell and Hall, 1997, 2002). At this moderate temperature the acetate reaction had to be catalyzed (Shock et al., 1998). Mackinawite (FeS) and greigite ($NiFe_5S_8$) nanocrysts comprising the first membranes are significant in this respect, and plausible evolutionary steps may be imagined between these and the fully fledged enzymes with [$NiFe_4S_5$] centers involved in the generation of acetate to this day (Russell and Martin, 2004). Energy from the acetate reaction, augmented by a natural protonmotive force, the consequence of the pH and redox gradients acting across the semiconducting and semipermeable membrane, was coupled to the formation of pyrophosphate. In turn the energy in the phosphate bond drove polymerization. Small quantities of amino acids, metal-bearing clusters, and eventually RNA precursors, self-organized to become involved in the more efficient generation of peptides and acetate waste, a thermodynamic

imperative. RNA genetic regulators eventually evolved to the state where they could be passed on to offspring and be shared with their neighbors (Mellersh, 1993; Hanczyc et al., 2003; Koonin and Martin, 2005). Amyloidal peptides and other polymers eventually took over from iron sulfides as membrane and cell wall constituents.

Pressurized microflow and circulation reactors could be used in parallel and series to test these aspects of the model (Russell et al., 2003; Braun and Libchaber, 2004).

The first gene-swapping cellular cooperative would have emerged at moderate temperature where chemical and electrochemical gradients were high near the surface of the mound. These acetogenic cells were the ancestors of the Bacteria, organisms that evolved while still within the mound to use electron acceptors other than CO_2 and Fe^{III}, perhaps in the order Mn^{IV} and S^0 (Baymann et al., 2001). But free energy was also to be had deeper within the mound where temperatures were higher, though gradients may have been lower. Here a small number of cells may have been able to withstand higher temperatures where the methane reaction was favored. Eventually specializing in generating methane waste, these methanogenic cells differentiated from the parent population (the last common community) to become the forerunners of the Archaea, the second domain of prokaryotic life (Martin and Russell, 2003). Both the Bacteria and the Archaea expanded into environments offering comparable conditions. Although nutrient supply was at a premium, only the oceanic sediments and crust could support these early vulnerable communities. Living syntrophically, the prokaryotes inaugurated the deep biosphere, well out of the way of the early and late bombardments (Parkes et al., 1990). Here they developed the capacity to use SO_4^{2-} and N_2 as electron acceptors.

Convection remained a driving force for evolution. At a large scale, plate tectonics drove portions of the deep biosphere into the photic zone on ocean island chains. Supplied with nutrients (e.g., H_2 and H_2S) and trace metals from subaerial hot springs (Ca, Fe, Mn, Ni, Co) and protected by chemical and detrital sediment, some of the Bacteria adapted the power of photons to drive electron transfer and thereby metabolism. The transition elements could be photo-oxidized, only to be re-reduced by organic molecules. Accumulation of ambient manganese within certain photosynthetic bacteria is likely to have protected them from UV injury (cf. Daly et al., 2004). Once within the cell, a ranciéite cluster [$CaMn_4O_9.3H_2O$] was co-opted to act as the oxygen evolving center [$CaMn_4$] ± $2H_2O$) which, indirectly excited by photons, extracted the hydrogen (as protons and electrons) from water. The protons and electrons were used in the reduction of CO_2 for biosynthesis while oxygen was emitted as waste. There is no compelling reason to assume life required billions of years to configure the process of oxygenic photosynthesis and several reasons to suppose that this biosynthetic pathway had emerged before our stratigraphic record began ca. 3.75 Ga (Rosing and Frei, 2004). It can therefore be inferred that the core metabolic cycles were in place by that time (Pace, 2002). Reaction with biogenic methane, the use of oxygen as an electron acceptor, and the oxidation of ferrous iron kept oxygen concentrations vanishingly low until the early Proterozoic (Lécuyer and Ricard, 1999; Catling et al., 2001).

Although compartmentalized, the biosphere overall is autotrophic. Bernal (1960) put it well: "Life, geologically speaking, consists of the interference with secondary lithosphere-atmosphere reactions so as to produce a small but ever-renewed stock of organic molecules." Energized mainly by the sun's rays, the two essential contributors to this stock are (i) hydrogen, gained for the most part from water through photosynthesis with a minor component released during the hydrous oxidation of ferrous iron, and (ii) carbon dioxide released during volcanism, metamorphism, subduction, and reoxidation or fermentation of biogenic detritus. Of course there are all kinds of continuing interactions between the biosphere and lithosphere. However, we can conclude that the autogenic view of the emergence of life posed here sits well with the way the biosphere operates, and operated, right from its inception.

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