Introduction

LEDUCE’S (1911) profound advice on the study of life and its beginnings also holds for many mineral deposits, particularly those generated at hot springs on, or just beneath, the sea floor. In his seminal paper of 1968 Donald White considered the genesis of ore deposits to involve four critical aspects: (1) a source for the ore constituents; (2) concentration of these and other incidental constituents in a hydrous phase; (3) the migration of this fluid in, for example, balanced convection; and (4) selective precipitation of the ore constituents in response to chemical and physical change as the fluid migrates into new environments. We adopt the same approach in our investigation into the emergence of life. Once life had emerged, its waste products had a major aspect: (1) a source for the ore constituents; (2) concentration of these and other incidental constituents in a hydrous phase; (3) the migration of this fluid in, for example, balanced convection; and (4) selective precipitation of the ore constituents in response to chemical and physical change as the fluid migrates into new environments. We adopt the same approach in our investigation into the emergence of life. Once life had emerged, its waste products had a major aspect: (1) a source for the ore constituents; (2) concentration of these and other incidental constituents in a hydrous phase; (3) the migration of this fluid in, for example, balanced convection; and (4) selective precipitation of the ore constituents in response to chemical and physical change as the fluid migrates into new environments. We adopt the same approach in our investigation into the emergence of life. 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influence on our planet’s hydrosphere and atmosphere over time (e.g., Canfield, 1998; Martin et al., 2003). These products also contributed to the generation and survival of many metallic ores.

For the energy and materials of a hydrothermal convection cell to result in the precipitation of ore, the fluid must have been physically confined immediately prior to dissipation to the wider environment. Similarly, the precursor molecules of life must also have been concentrated. Containment of products was all-important for both processes. For submarine ore deposition containment could have been effected by a reactive layer, a cap rock of low permeability, an anhydrite baffle, a trap such as the halocline above a brine pool, or merely by the imposition of a steep temperature gradient. For very earliest life, the containment of biochemical feedback cycles was effected by a membrane, a capping layer that has since evolved from an iron sulfide precursor to become a lipid/protein complex in present day cells. Thus sulfur, required for the deposition of so many ores, was, we suggest here, also a necessary contributor to emergent life. Apart from energy and containment, what were the other requirements of emergent life?

To address its material sources it helps to consider life in a simple formula, i.e., $[C_{70}H_{129}O_{65}N_{10}P(\text{Fe, Ni, Co, Zn, Mo})S]$ (cf. Redfield et al., 1963; Orr, 1978; Morel and Hudson, 1985; Fagerbakke et al., 1996; Macalady and Banfield, 2003). Although the formula overrepresents the metals and sulfur in today’s organisms, it reflects the notion that “it is the inorganic elements that bring organic chemistry to life” (D. Garner, pers. commun., 1994). Even in modern proteins, 50 percent of the active centers consist of a metal ion or metal clusters (Jernigan et al., 1994). Iron, zinc, nickel, cobalt, molybdenum, manganese, sulfur—typical constituents of many mineral deposits—are particularly important in enzymes, which are catalysts for many of life’s processes.

But where did the energy come from to drive the emergence of life and maintain it? One obvious candidate was the sun. However, less than a volt is required to drive life’s electrochemical processes. Indeed, many nonphotosynthetic bacteria survive on 250 mV or thereabouts (Thauer et al., 1977), and a continuous potential exceeding a volt would electrocute a single unprotected living cell. So protective measures against the bond-breaking effects of the UV-radiating young sun (middle UV radiation has a potential of ~5 V) had to be developed before solar energy could be directly exploited. A hydrothermal source of chemical energy seems more promising and was suggested as early as 1981 by Corliss, Barross, and Hoffman. Black smokers were their favored site for the origin of life (Corliss et al., 1981). But, given the fragility of RNA (Table 1), life is now considered unlikely to have emerged at much above 40°C (Forterre and Philippe, 1999; Reysenbach et al., 1999; Moulton et al., 2000). Moreover sulfides, which are thought to have provided catalytic surfaces, could not have precipitated from acid high-temperature solutions exhaling into a rather acidic and reduced ocean (Maisonneuve, 1982).

Thus a moderate-temperature hydrothermal system that focused not only the requisite energy but also all the primary materials needed to build cells was a more likely site for life’s emergence. Supply must have been at relatively constant rates, at rather low temperature, and buffered against low pH (i.e., the system must have behaved as a natural thermostat and chemostat). Of equal importance, the system must have been able to get rid of its wastes. In this paper, we concentrate not so much on what life is but on what life does (Russell and Hall, 1997); life produces low-grade heat and waste chemicals. It has been argued that an off-ridge submarine alkaline hydrothermal system fulfills all these criteria, i.e., that the outputs of such a system were the inputs to the first metabolizing cells (Russell et al., 1989, 2003; Shock, 1992; Russell and Martin, 2004).

We suggest the modulated interactions between the alkaline hydrothermal solution and acidulous ocean water, near and at the surface of a hydrothermal mound and across hydrothermally precipitated coagulations, created the conditions suitable for the reduction of CO$_2$, that is, for the synthesis of organic molecules on site, a primitive metabolism, and the onset of life. Such low-temperature hydrothermal systems are not known for their associated mineral deposits, although where they circulated within ultramafic rocks and exhaled into lakes and subaerial environments, magnesite and hydro-magnesite deposits have formed and, in places, are forming still (Fallick et al., 1991; Zedef et al., 2000). Indeed, it was the study of Alpine magnesite deposits, as well as of the moderate-temperature Irish base metal deposits, that led to the hydrothermal model for the emergence of life that we present below. This model may be characterized as autogenic in that it assumes CO$_2$ rather than preformed organic molecules to be the main source of carbon.

A model presented by Wächtershäuser (1988a, b) is also autogenic and also involves iron sulfides. Wächtershäuser’s theory invokes a single-pass acidic “CO$_2$-laden volcanic exhalation,” CO$_2$ which is supposedly reduced on a growing pyrite surface generated from ferrous iron and hydrogen sulfide. The putative organic molecules produced in this way are presumed to self-organize and detach from the two-dimensional surface to form the first metabolizing cell. A series of experiments under these conditions has resulted in the formation of methyl sulfide (CH$_3$S$^-$; Heinen and Lauwers, 1996), acetate (CH$_3$COO$^-$; Huber and Wächtershäuser, 1997), amino acids (Huber and Wächtershäuser, 2003), and short amino-acid polymers, i.e., peptides (Huber and Wächtershäuser, 1998), although not lipids, the constituents of microbial and other membranes. Of particular significance in Wächtershäuser’s later experiments was the use of freshly precipitated iron and nickel sulfides as catalysts and a buffering of pH at around 9 to achieve high yields of peptides (Huber and Wächtershäuser, 1998, 2003).

In contrast to the Wächtershäuser model, our hypothesis relies on an alkaline H$_2$-bearing hydrothermal solution reacting with a CO$_2$-bearing ocean in three-dimensional compartments walled by iron sulfides. Our model accepts that the formation of pyrite may be required to produce methyl sulfide (Heinen and Lauwers, 1996), but it also provides a plausible geochemical environment for the iron-sulfur interactions envisaged by ourselves and by Wächtershäuser, yet a more diverse range of reaction sites and conditions at which prebiotic syntheses could occur. Cody (2004) has recently compared these two models in his review of the place of transition metal sulfides in the origin of metabolism.

Organotrophic or plasmogenic models, i.e., those assuming that a plethora of organic molecules were available on the
### Table 1. Glossary

<table>
<thead>
<tr>
<th>Standard biochemical terms</th>
<th>Definition</th>
<th>Notes</th>
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<tbody>
<tr>
<td>Activated hydrogen</td>
<td>A short-lived, highly reactive state of hydrogen</td>
<td>Consists of hydrogen atom with a single electron e.g., a pyrophosphate bond ADP needs chemical energy (via metabolic processes) to return to ATP The side chain influences the properties of the amino acid ATP can drive a multitude of biochemical reactions, e.g., polymerizations by the removal of the constituents of H2O Conventionaly such molecules are termed either left or right handed DNA (and RNA) are characterized by a “sequence” of bases; groups of three consecutive bases are known as “codons”; groups of codons are called genes which control the biosynthesis of proteins The overall shape of an enzyme partly controls its catalytic properties; metallic cations bonded within proteins often also influence their biochemical role The variable valence states of iron contribute to the electrophysical and/or biochemical role of ferredoxins Polymers may be heterochiral</td>
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<tr>
<td>Anhydride bond</td>
<td>A bond formed by the elimination of the constituents of water</td>
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<td>ADP</td>
<td>The energy-depleted molecule, Adenosine DiPhosphate</td>
<td></td>
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<tr>
<td>Amino acid</td>
<td>A molecule with general formula NH2-CHR-COOH, where “R” is a side chain</td>
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<tr>
<td>ATP</td>
<td>The energy-rich molecule, Adenosine TriPhosphate, consisting of the nucleic acid base, adenosine, and 3 consecutive phosphate groups</td>
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<tr>
<td>Chirality</td>
<td>The noncongruence of molecules with their mirror image</td>
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<tr>
<td>DNA</td>
<td>DeoxyriboNucleic Acid is a long molecule of 2 adjacent chains (twisted in a double helix), each consisting of a sequence of nucleotides which consist of a base and a sugar-phosphate which forms a “backbone” to the chain</td>
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<tr>
<td>Enzyme</td>
<td>A large protein molecule which catalyses one or more biochemical reactions</td>
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<tr>
<td>Ferredoxin</td>
<td>An enzyme that contains an iron-sulfur ionic center</td>
<td></td>
</tr>
<tr>
<td>Heterochiral</td>
<td>Of mixed chirality</td>
<td>e.g., RNA monomers NAD and NADP (with additional phosphate) can carry hydrogen (chemical energy) in reduced and oxidized forms, i.e., NADH and NAD+; also, NAD can remove H from C-OH to make C=O bonds ATG only occur in DNA and AUGC only in RNA</td>
</tr>
<tr>
<td>Heterotroph (or organotroph)</td>
<td>An organism requiring a source of organic carbon for biosynthesis</td>
<td>The peptide bond results when amino (-NH2) and carboxyl (-COOH) groups of two amino acids react by extraction of the constituents of a water molecule The “sequence” of amino acids characterizes a protein and controls its biochemical role The pmf drives the formation of “high-energy” bonds between phosphate to produce pyrophosphate (cf. chemiosmosis)</td>
</tr>
<tr>
<td>Lithotroph (or autotroph)</td>
<td>An organism that uses CO2 as its sole source of organic carbon, and other simple inorganic constituents such as hydrogen, ammonia and inorganic phosphate</td>
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<tr>
<td>Monomer</td>
<td>A single molecule that contributes to a molecular chain (polymer)</td>
<td>NAD and NADP (with additional phosphate) can carry hydrogen (chemical energy) in reduced and oxidized forms, i.e., NADH and NAD+; also, NAD can remove H from C-OH to make C=O bonds ATG only occur in DNA and AUGC only in RNA</td>
</tr>
<tr>
<td>NAD</td>
<td>A Dinucleotide molecule: Nicotinamide (C,N-ring molecule with amino-acid-like side chain) and Adenine (Adenosine base with 2 ribose sugars linked by two phosphates)</td>
<td></td>
</tr>
<tr>
<td>Nucleic acid bases</td>
<td>The five bases (ring structures of C, N, H, O) are adenine (A), thymine (T), guanine (G), cytosine (C), and Uracil (U)</td>
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<tr>
<td>Nucleotide</td>
<td>An individual nucleic acid comprising a nitrogenous ringed base, a ribose or deoxyribose sugar, and a phosphate</td>
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<td>Organophosphates</td>
<td>A general term for organic molecules which contain P usually within a phosphate group (PO4)3-</td>
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<tr>
<td>Peptide (strictly polypeptide)</td>
<td>A chain of amino acids linked by peptide bonds which are also known as amide bonds</td>
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<tr>
<td>Protein</td>
<td>Proteins are long chains made from an inventory of 20 amino acids in current living systems</td>
<td></td>
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<tr>
<td>Promototive force (pmf)</td>
<td>Protons moving downgradient through the membrane can do work</td>
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<tr>
<td>Racemic</td>
<td>A mixture of a particular chiral molecule in which the left- and right-handed varieties are in equal proportion</td>
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<tr>
<td>RNA</td>
<td>RiboNucleicAcid has the same style of structure as DNA</td>
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<tr>
<td>Siderophore</td>
<td>A ligand with a high affinity for FeIII attached to a short heterochiral chain of amino acids</td>
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<tr>
<td>Sugars</td>
<td>Compounds that contain only carbon, hydrogen, and oxygen, usually in a ring structure of 5 or 6 carbons</td>
<td>DNA contains a relatively reduced sugar molecule (Deoxyribose) and RNA, a relatively oxidized sugar molecule (Ribose) the difference being an -H group in deoxyR and an -OH group in R Produced by bacteria to acquire iron Glucose is a 6C-ring sugar (C6H12O6) and is an important energy reservoir for metabolism because of high energy C-C bonds. Ribose and Deoxyribose have SC ring structures</td>
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<tr>
<td>Syntrophy</td>
<td>The collaboration of organisms in degrading a substrate that is otherwise resistant</td>
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<tr>
<td>Emergence of life terms and/or phrases</td>
<td>Explanation</td>
<td></td>
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<tr>
<td>Acidulous</td>
<td>Mildly acidic</td>
<td>Originating from inorganic molecules</td>
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<tr>
<td>Autogenesis or abiogenesis</td>
<td>A term that implies that there is a sequence of stages whereby a chemical system attains new properties during its evolution from the abiological to the biological</td>
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<tr>
<td>Emergence of life</td>
<td>A term that implies that living biological systems started as the energy requirements for a regulated metabolism were first met (cf. the onset of convection)</td>
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<tr>
<td>Onset of life</td>
<td>A term that implies that living biological systems started as the energy requirements for a regulated metabolism were first met (cf. the onset of convection)</td>
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<tr>
<td>Plasmogensis</td>
<td>Originating from preformed organic molecules, such as proteins and lipids suspended in an aqueous fluid</td>
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<tr>
<td>Primitive polymerase</td>
<td>A catalyst of polymerization</td>
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<tr>
<td>Protoferredoxin</td>
<td>A chemical imagined to exist as a precursor before modern biosynthesized ferredoxins</td>
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<tr>
<td>RNA instructors</td>
<td>Sequences of RNA that control the molecular sequence of the amino acids comprising a peptide</td>
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<tr>
<td>Thermophoresis</td>
<td>The movement of particles (e.g., DNA) against a temperature gradient from hot to cold</td>
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<tr>
<td>Useful amino-acid sequences</td>
<td>Sequences of amino acids that enhance catalytic efficiency</td>
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</table>
early Earth to act as fuel, substrate, and membranes for the first organisms, became popular from the 1920s onward (Oparin, 1924, 1938; Haldane, 1929; Miller and Urey, 1959; Fox et al., 1962). These models displaced the earlier autogenous ideas of Darwin (in F. Darwin, 1888), Haeckel (1892), and Leduc (1911) and vied with Goldschmidt’s (1952) principles. Organotrophic theorists need now to account for the “lipid” and “RNA worlds” in which the simple organic building components of life are thought to have been continually derived from extraterrestrial or atmospheric sources (Deamer, 1985; Gilbert, 1986; Orgel, 1986; Joyce, 1989). But the mechanisms by which delicate molecules such as RNA (ribonucleic acid, Table 1) may have been recovered from these putative sources upon a tempestuous Earth and then selected for by the earliest organisms has been left undressed (e.g., Nilson, 2002; cf. Cody, 2004). Badia (2004) is the latest advocate of the organotrophic hypothesis.

In this contribution we trace what we consider to be a likely evolutionary path from the geochemistry of hydrothermal systems to the emergence of life and the first diverging biochemistries. In this scenario, hydrothermal convection cells contribute energy and materials to ore formation and life alike. Indeed, once bacteria had evolved, they played a large part in the deposition of ores of sedimentary exhalative affiliation.

The Early Earth

The early ocean was likely to have been at least partially vaporized many times by massive meteorite impacts in the first half billion years or so of Earth history. The dust clouds and sulfate aerosols produced by these impacts and by micrometeorites may have counterbalanced the carbon dioxide greenhouse gas and reflected sunlight back to space to effect rapid cooling to ≤20°C (Hunten et al., 1980; Godderis and Veizer, 2000; Maurette et al., 2004). At that time, the sun had only about 70 percent of its present luminosity although, in the absence of an ozone layer, the UV flux was nearly an order of magnitude higher (Canuto et al., 1982; Kasting, 1990; Bahcall et al., 2001). After the solar wind blew away the primary atmosphere, the H2, CO2, SO2, P2O10, and N2 degassed through volcanoes or introduced by micrometeorites and comets were trapped gravitationally to comprise the volatisphere (Goldschmidt, 1952; Yamagata et al., 1991). Any reduced gases, such as CO, CH4, and H2S, were rapidly oxidized by the hydroxyl radical generated by the photolysis of water vapor in atmosphere (Kasting, 1993; Kelley and Früh-Green, 1999; Scott et al., 2004). The partial pressure of CO2 in this secondary atmosphere has been estimated as anywhere between 0.2 and 10 atmospheres (Walker, 1985; Kasting, 1990). In contrast the partial pressure of oxygen was generally extremely low (Kasting, 1993; Pavlov and Kasting, 2002).

Although the sialic continents had probably differentiated by the end of the Hadean (~3.8 Ga), there were no landmasses to speak of, because the continental crust was highly radioactive, hot, and pliable and therefore too weak to stack up above the ocean surface (Armstrong, 1981; Russell and Arndt, 2005). In the absence of significant land, and with the moon much closer than today, the ocean surface of the rapidly rotating Earth would have been strongly affected by tornadoes and water spouts, returning surface solutes and any organic molecules (i.e., molecules that may have survived delivery from space) to the atmosphere where they would also have been photo-oxidized. Without the buffering and stabilizing effects of landmasses and life, the state of the Hadean atmosphere, both physical and chemical, would have been highly turbulent and changeable. Suggestions that life originated from organic slicks upon the ocean surface—slicks derived from carbonaceous micrometeorites or supposedly exuded from the Earth’s interior—take no account of these initial, hostile conditions (Deamer, 1985; Cleaves and Miller, 1998; Nilson, 2002; Ric ard o et al., 2004). Also, bodies of fresh water, if any, would have been ephemeral in these violent times. The “warm little pond” favored by Darwin as a cradle of life (Darwin, 1888) could not have been realized (Maher and Stevenson, 1988; Godderis and Veizer, 2000; Kamber et al., 2001).

Radioactive heat production within the Earth’s mantle during the first few hundred million years was high and exceeded present production more than five-fold (Turcotte, 1980). Mantle convection must have culminated in a rapid production of ~30-km-thick oceanic crust (Sleep and Windley, 1982; Arndt and Chauvel, 1990; Arndt, 1998). Given the high temperatures of magma generation then, a proportion of the ocean floor would have comprised ultramafic volcanic rocks (i.e., komatiites), as well as basalts, overlying mafic, and ultramafic cumulates (Fig. 1). Concomitant destruction of crust occurred at convective downdrafts only a few hundred kilometers from the spreading centers (Abbott and Hoffman, 1984).

High-temperature submarine hydrothermal convection cells dissipated heat from all these zones. Even by the Late Archean, hydrothermal activity is estimated to have been three times that of the present day (Isley and Abbott, 1999). Lower temperature springs and seepages would have been widespread on ridge flanks and in the quieter conditions of the deep Hadean ocean floor (Russell et al., 1988; Shock, 1992). The lower temperature springs and seepages focused a strong chemical disequilibrium at the ocean floor that, we argue, played an important role in the emergence of life through the coupling of redox and acid-base reactions controlled at first through an inorganic membrane (Russell et al., 1994: Fig. 2). The significance of these submarine hydrothermal systems to the emergence of life is examined in the next section.

Two Classes of Submarine Hot Springs

The convection of ocean water in fractured rock transferred heat from the fresh hot crust, in a myriad of convection cells, to the intermittently cool Hadean ocean where, ultimately, it was radiated to the cold sink of space. Hydrothermal convection cells, sourced from the ocean and operating in oceanic crust, then as now, organized themselves into two main distinct classes as described below. The ratio of very hot springs to those of moderate temperature would have been greater than today; a consequence of higher magmatic intrusion and extrusion rates. Slow-moving hydrothermal convection and advection currents also would have operated within the ocean floor at temperatures of up to 20°C or so (Anderson et al., 1977; Herzig and Hannington, 2000) but are not considered further as they would have had little overall chemical effect.
Chemosynthetic life may have emerged at a warm alkaline seepage and expanded into the surrounding sediments and crust. The transition elements catalyzing the reduction of CO₂ in the alkaline mound were derived from high-temperature springs emanating from constructive plate boundaries and the apices of plumes. At times and in places it is possible that convection involved the whole mantle.

FIG. 2. Model environment for the emergence of life at a submarine seepage on the ocean floor (Russell and Hall, 1997; Russell and Martin, 2004). Here, a hydrothermal mound (see insets) acted as a self-restoring flow reactor and fractionation column. In it hydrothermal hydrogen and ammonia reacted with bicarbonate and phosphate derived from the ocean to synthesize organic molecules, e.g., acetate, amino acids, and minor RNA. Iron and/or nickel sulfides in the gelatinous and membranous froth acted as the catalysts and with absorbed amino acids, as protoferredoxins. Much of the acetate was exhaled as waste but a proportion of it, and of the amino acids, was retained. These amino acids organized themselves into an early system of biochemistry, i.e., protolife.
High-temperature systems (≥350°C) in mafic and ultramafic hosts

High-temperature, hydrothermal convection at oceanic spreading centers, present and past, is now a phenomenon familiar to all economic geologists. In open convective systems driven by magmatic intrusion, the average upper temperature is controlled either by the buoyancy of supercritical water, which is dampened significantly at high pressure, or by the permeability of volcanic rock, itself dependent on temperature (Cathles, 1983, 1990; Bischoff and Rosenbauer, 1985; Schultz and Elderfield, 1997). Barrie et al. (2001) estimate that, when intruded by magma, komatiitic rock becomes permeable to circulating seawater only below 475°C. The chemistry of the high-temperature solutions is buffered by water-rock interactions, although magmatic volatiles at much higher initial temperatures also can make a contribution (de Ronde, 1995). The duration of such systems can exceed 100,000 yr (e.g., Lalou et al., 1993). High-temperature systems, then and now, were rendered acidic (pH ~3) as ocean water in the downflow, serpentinitized mafic rock at high temperature (Seyfried and Bischoff, 1981; Donville et al., 2002).

Acidic solutions can dissolve transition and base metals from sulfides and silicates comprising the crust (Von Damm, 2000; Donville et al., 2002; Allen and Seyfried, 2003). Products of such fluids are similar to the copper-zinc ores of Cyprus (Constantinou and Govett, 1973; Hannington et al., 1998). Here fragments of pyritic chimneys constitute a portion of the ore just as they do in deposits presently forming on the mid-Atlantic Ridge (Oudin and Constantinou, 1984; Humphris et al., 1995; Zierenberg et al., 1998; Hannington et al., 2001).

Sulfate concentrations in the Archean ocean are known to have been low, although there is no information from the Hadean (Farquhar et al., 2001). Micrometeorites with a sulfur content of ~5 percent would have contributed, upon photo-oxidation, about 10^{16} g/yr of SO_{2} to the atmosphere during the first 100 m.y. or so of Earth’s history. Rapidly transformed to aerosol particles, the resulting sulfate and native sulfur would have been rained out into the earliest Hadean ocean (Farquhar et al., 2001; Maurette et al., 2004). Much of the sulfate would have been removed by high-temperature water-rock reaction. Magnesium and sulfate reacted with ocean (Farquhar et al., 2001; Maurette et al., 2004). Much of the sulfate would have been removed by high-temperature water-rock reaction. Magnesium and sulfate reacted with sea-water to gravitate down to several kilometers. As it made its tortuous way through the somewhat altered mafic and ultramafic oceanic crust, further exothermic hydration, carbonation, and oxidation reactions chemically modified this water so that a tiny fraction was partially reduced to H_{2}, as it was in the high-temperature springs. In the absence of magmatic heat, complete serpentinitization and oxidation of orthopyroxene at these low temperatures would have produced silica and magnetite with the release of H_{2} and OH:

\[ 6MgFeSiO_{3} + 13H_{2}O \rightarrow Mg_{5}Si_{2}O_{5}(OH)_{4} + 4SiO_{2} + 2Fe_{2}O_{3} + 3Mg^{2+} + 6OH^{-} + 8H_{2}, \quad (3) \]

and calcium dissolution from diopside would also have produced serpentine and led to an even higher pH (Neal and Stanger, 1984; Palandri and Reed, 2004):

\[ 12Ca_{0.28}Mg_{0.72}Fe_{0.25}Si_{2}O_{6} + 16H_{2}O \rightarrow 6Mg_{5}Si_{2}O_{5}(OH)_{4} + 12SiO_{2} + 2Fe_{2}O_{3} + 3Ca^{2+} + 6OH^{-} + H_{2}↑. \quad (4) \]

Such serpentinitization would have increased markedly at around 85°C (Wedner and Taylor, 1971; Macleod et al., 1994; Lowell and Rona, 2002). The increase of rock volume brought about by serpentinitization may have closed fractures at about 115°C in the absence of igneous intrusion (Wedner and Taylor, 1971), although tidal and tectonic flexure would have produced new fractures to expose fresh rock to the circulating fluids. Iron-nickel alloys in such rocks (Krishnaraao 1964) would have acted as reducing agents and catalysts for abiogenic production of millimolar quantities of CH_{3}S^{-} and NH_{3} as well as micromolar quantities of CN^{-} (Shock and Schultz, 1998).

Alkaline springs similar to those predicted for the Hadean (Russell et al., 1989, 1998) have been operating for the last 30,000 yr or more in 1.5-m.y.-old 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). As expected, the pH of these fluids is around 10, and their temperature at exhalation is 70° to 75°C. Comparable also is a fresh-water–charged, warm (72°C) alkaline (pH 10) submarine spring discovered off the coast of Iceland characterized by porous conical mounds of Mg-rich clay tens of meters high (Marineinson et al., 2001; Gepert et al., 2002).
Ocean Water, the Hot Spring Sink

In the absence of subaerial continents, Hadean ocean chemistry would have been dominated by atmospheric CO\textsubscript{2} and the exhalations from the two main classes of hydrothermal spring. A carbonic (pH 5–6) and reduced Hadean ocean was a reservoir for transition elements contributed from the magma-driven hot acidic springs. These springs could contribute \(-20 \text{ mM/l of Fe}^{2+}\) to the ocean, by analogy to modern vents. Dilution and reaction with the cooler, less vigorous alkaline springs would have lowered these values, but we assume a concentration approaching 10 mM/l could have been attained, at least at times. Some indication of the carrying capacity of the ocean is given by Fe\textsuperscript{2+} of windblown derivation in the carbonic lakes in Cameroon (pH \textasciitilde 5.5). Here Fe\textsuperscript{2+} concentrations are between 10 and 20 mM/l (Sigurdsson et al., 1987; Kling et al., 1989). Some of the Fe\textsuperscript{2+} would have been photo-oxidized to FeOOH at the surface of the Hadean ocean (Braterman et al., 1983). The ferric iron flocculant would have acted as a dispersed positive electrode in the Hadean ocean, a kind of “borrowed light” helping to energize the emergence of life (Cairns-Smith et al., 1992; Fig. 2).

Although the Hadean ocean is generally agreed to have been acidulous, its temperature is less well constrained. It is likely to have varied widely from well over 100°C after meteorite impacts and when CO\textsubscript{2} concentrations were particularly high, to near freezing when atmospheric and galactic dust clouds and aerosols absorbed solar radiation.

Given these conditions, we can now investigate how reaction between the \(-110°C\) alkaline springs and the cooler ocean could have led to life’s emergence.

The Alkaline Hydrothermal Mound—A Natural Flow Reactor

A mound comprising Mg-rich clays, ephemeral carbonates, green rust, and sulfides would have formed where the alkaline hydrothermal solutions exhaled into the carbonic Hadean ocean (Russell and Hall, 1997, 2002; Russell and Martin 2004). In this section we explain how this hydrothermal mound acted as a natural, self-restoring flow reactor in which the dissolved volatiles furthest from equilibrium—H\textsubscript{2} and NH\textsubscript{3} in hydrothermal solution, and CO\textsubscript{2} and HP\textsubscript{2}O\textsubscript{7}\textsuperscript{3–} in the ocean—may have reacted to form simple organic molecules. Because the temperature and chemistry of the hydrothermal system were buffered by the mafic to ultramafic nature of the oceanic crust, the products were relatively uniform over time. The main reactions would have taken place at the margins of the mound where the thermal, chemical, and electrochemical gradients were steepest. The margins of the mound acted as a semipermeable and semiconducting barrier between the hydrothermal solution and ocean water, thereby controlling their interaction.

Where the convective upflow was vigorous in the ancient crust, the alkaline spring waters (pH \textasciitilde 10, \textasciitilde 110°C) would have exhaled directly into the cool acidulous ocean (pH \textasciitilde 5.5, \textasciitilde 20°C; Russell et al., 1989; Shock, 1992; Macleod et al., 1994; Fig. 2). In time, reaction of hydrothermal hydroxyl (OH\textsuperscript{–}) and hydrosulfide (HS\textsuperscript{–}) with Fe\textsuperscript{2+} from the ocean contributed to the formation of mounds and spires (Figs. 2, 3, 4). As the fracture conduits in the mounds became clogged with gels comprised of silica, carbonate, saponite, brucite, green rust, and iron sulfide, the discharge became diffuse and seepages replaced springs (Figs. 4, 5). Such restraint would have favored the formation of membranes of FeS and/or FeOOH, depending on the composition and local pH of the fluids (Fig. 5). Any such semipermeable and semiconducting membranes, as well as rapidly precipitated internal dendrites, would have provided solid surfaces for further chemical interactions between reactive solutes. Only ionized and strongly polar molecules such as the cyanide ion (CN\textsuperscript{–}) and the polar formaldehyde (H\textsubscript{2}CO) would have been adsorbed in the mound and on FeS/Fe\textsubscript{3}S\textsubscript{4} membranes and thereby retained (Leja, 1982; Rickard et al., 2001).

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**Fig. 3.** a. Pyrite botryoids (bubbles) formed a surface at a 350 Ma warm spring feeding part of the Tynagh lead-zinc deposit, Ireland. b. A natural “chemical garden” (Russell, 1988) from Tynagh comprising pyrite spires (gray) embedded in coarse barite (white). The darker material surrounding the pyrite core (arrowed) is largely tennantite. Pyrite is presumed to have replaced iron monosulfide membranes in both cases (Ranks, 1985; Russell, 1988). These structures formed (originally as membranous FeS) as acidic iron-bearing hydrothermal solutions met and reacted with alkaline brines, the inverse of conditions at an off-ridge submarine seepage in the Hadean (Russell, 1988). Continually inflated with hydrothermal solution, the membranous barrier separating the two solutions failed repeatedly but was instantly healed with new precipitates of FeS. The unstable FeS is now pyrite, FeS\textsubscript{2} (compare with Fig. 4).
Hollow botryoids of iron sulfide found at the exhalative lead-zinc orebody at Tynagh in Ireland inspired the idea that life emerged and evolved in microcavities or cells composed of FeS precipitates (Russell et al., 1988, 1989; Fig. 3). However, at the interpreted temperatures of formation of up to 250°C, the type of mineralizing fluids responsible for the Irish mineral deposits would have destroyed fledgling organic polymers rather than contributed to their synthesis (Banks and Russell, 1992; Bada and Lazcano, 2002). Lower temperature examples of springs and seepages that were alkaline rather than acidic and that contained hydrogen (Neal and Stanger, 1984) may be represented by the Alpine magnesite deposits described in Fallick et al. (1991) and Zedef et al. (2000). Although sulfide compartments were not a feature of such deposits we reasoned that they might have formed in the Hadean ocean because of the capacity of the reducing environment to encourage the synthesis of acetate (reaction 7). Here the energy produced by acetate production may have helped to drive the synthesis of other organic molecules on a local scale (Russell and Martin, 2004; Fig. 4). These by-products would have included amino acids, especially glycine (NH2·CH2·COO−; Hennet et al., 1992), and a much smaller proportion of nucleic acids. The reaction that produces waste acetate (H3C·COOH)−, water, and the organic molecules that constituted a protolife can be summarized notionally as:

\[407\text{H}_2 + 10\text{NH}_3 + \text{HS}^- \text{hydrothermal} + \\
\{210\text{CO}_2 + \text{H}_2\text{PO}_4^- + \{\text{Fe, Ni, Co, Zn, Mo}\}^{2+}\}_\text{ocean} \rightarrow \\
\{\text{C}_{70}\text{H}_{165}\text{O}_{66}\text{N}_{10}\text{P}(\text{Fe, Ni, Co, Zn, Mo})\}_\text{protolife} + \\
\{70\text{H}_3\text{C·COOH} + 219\text{H}_2\text{O}\}_\text{waste}. \] 

Both minerals contain some nickel, although mackinawite is the likely metastable precipitate in the conditions we propose for the emergence of life.

In our model, the hydrothermal mound acts as a reactor in which the putative organic precursor molecules to life would be generated, along with and contingent upon, the precipitation of metastable iron-nickel sulfide gels and nanometric mackinawite \([\{\text{FeNi,Co}\}^{+} \text{S}]\) and greigite \((\text{NiFe}_2\text{S}_5)\) membranes. The ~110°C alkaline hydrothermal fluid directly supplied the reduced chemical species such as HS− and chemical reaction for the production of methane (CH4) and acetate (H3C·COO−) as hydrothermal fluid mixes with mildly oxidized ocean water. Although the strongest thermodynamic drive is to the production of CH4 as aqueous CO2 reacts with hydrothermal H2, kinetic barriers prevent reaction below 500°C. And, even though the less reduced acetate becomes thermodynamically favorable below 60°C, kinetic barriers are still too high to permit its spontaneous synthesis (Shock et al., 1998; Schink, 1997):

\[4\text{H}_2 + 2\text{CO}_2 \rightarrow \text{CH}_3\text{·COOH} + 2\text{H}_2\text{O}. \] 

However, the acetate reaction is catalyzed in autotrophic living cells by metalloenzymes and vitamins (Thauer, 1998). Thus we might expect inorganic catalysts capable of promoting organic synthesis at the dawn of life to be comparable to the active centers of the metalloenzymes, i.e., sulfides of iron with ancillary nickel. As we have seen, such sulfides were a feature of hydrothermal mounds. Dissolved Fe2+ reacts with H2S (reaction 6) or HS− to produce the monosulfide pyrrhotite at high temperature and disordered mackinawite at low temperature (Fig. 6a; Vaughan, 1969; Morse and Arakaki, 1993; Wolthers et al., 2003):

\[\text{Fe}^{2+} + \text{H}_2\text{S} \rightarrow \text{FeS} + 2\text{H}^+. \] 

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FIG. 5.  a. A Pourbaix (Eh/pH) diagram illustrating the stabilities of siderite, mackinawite (FeS), pyrite, green rust, and hematite, produced for activities of $\text{H}_2\text{S}^{\text{aq}} = 10^{-3}$ and $\text{Fe}^{2+} = 10^{-6}$, using Geochemists Workbench (GWB, Bethke, 1996; Rahaman, 2002). The inset shows notional phase relations, emphasizing the intermediate oxidation state of the FeS component of membrane proteorhodanins, and is positioned to indicate the Eh-pH conditions pertaining to alkaline hydrothermal fluid as it entered Hadean seawater. Note the significant position of the pH boundary of monophosphate and/or polyphosphate with respect to the mackinawite/protophodanin/geigite redox boundary (cf. Fig. 8). Although computed for 120°C, this is now considered to be too high a temperature (see text). b. An Eh-pH diagram computed for modern atmospheric CO$_2$ to illustrate the impact of CO$_2$ on the hydrothermal precipitates; at higher pCO$_2$, the siderite field would expand as indicated by arrows but would contract at the lower pCO$_2$ of the pristine alkaline hydrothermal solution and would be replaced by mackinawite and green rust within the growing mound. The Fe$^{2+}$/Fe(OH)$_3$ boundary is projected (dashed line) to show its approximate position at very low pCO$_2$. Calculated using Geochemists Workbench (GWB, Bethke, 1996).

FIG. 6.  a. Structure of mackinawite, Fe$_{1+x}$S (Vaughan and Craig, 1978; Lennie and Vaughan, 1996; Wolthers et al., 2003). Mackinawite can be pictured as consisting of an assemblage of $[2\text{FeS}]$ rhombs (one such rhomb is shaded here for effect). The structure is arranged in such a way that it acts as a conductor in the basal plane and an insulator through the c axis. As such it may have acted as an electron transfer agent through, as well as main constituent of, the barrier separating hydrothermal fluid from ocean water—i.e., the first inorganic precipitate membrane or barrier (Russell and Hall, 1997; Russell et al., 1998). b. Supposed emergence of chemiosmosis (the protonmotive force) driven by reduction of Fe$^{3+}$ on the exterior of an FeS membrane. Electrons are conducted through mackinawite nanocrystallites from H$_2$, molecules which are dissociated to protons and activated hydrogen atoms (see Fig. 7) on the interior (Russell and Hall, 2002, cf. Ferris et al. 1992). Protons track electrons through aqueous films to conserve charge balance. The membrane potential is augmented by protons in the acidulous ocean and is an ambient protonmotive force sufficient to drive an emerging metabolism.
This C70 complex, approximating the formula of protolife as we imagine it, was a vital product generated on the mixing of hydrothermal fluid with Hadean ocean water (cf. White, 1968). However, life cannot be said to have emerged until the organic molecules retained in the mound became organized in RNA-controlled metabolic cycles within a cell surrounded by an organic membrane and cell wall. At first, ionic or polar organic products may have coated the interior of sulfide pores and bubbles. Eventually, organic polymers would have autonomously taken over the roles of cell membrane and cell wall. But how RNA became involved and organized amino-acid sequences in the first proteins within the cell membrane and interior is somewhat obscure, and a brief explanation is left to a later section. But when it did, the primitive living cells that differentiated within this reactor could be referred to as homoeoacetogens—cells that could grow lithotrophically from inorganic substrates just as acetogenic bacteria do today. A more detailed treatment of the hypothesis, and its evolutionary aspects, can be found in Russell and Hall (1997, 2002), Russell et al. (2003), Martin and Russell (2003), and Russell and Martin (2004).

The Organic Takeover

From catalysts to protoenzymes

The mackinawite and minor greigite nanocrysts that comprised the walls to the microcavities in our model acted as the catalytic surfaces for CO₂ reduction and acetate formation (Figs. 6, 7a). The structure of greigite (as Ni₅S₈-[Fe₄S₄]₂-Fe) (Vaughan and Craig, 1978) does share a similar conformation with the active centers of the enzyme lying at the base of the pathway that generates acetate and other organic molecules from CO₂ and a methyl group (Menon and Ragsdale, 2000; Dobbeck et al., 2001; Drennan et al., 2001; Doukov et al., 2002, Svetlitchnyi et al., 2004). This enzyme catalyzing acetate synthesis, known as carbon monoxide dehydrogenase/acetyl-CoA synthase (CODH/ACS), contains Ni/Fe active sites such as Ni₅Fe₅S₈ within the protein (Fig. 7c-e). The Fe₅S₈ clusters of greigite are assembled from Fe₂S₂ rhombs, and the same is probably true for the ferredoxins—“primitive” iron-sulfur electron transfer proteins (Eck and Dayhoff, 1966; Stevens and Kurtz 1985; D. Rickard, pers. commun., 2001; Fig. 7a, b).

![Fig. 7. Structural relatedness (emphasized by shading of the 2Fe2S rhomb component) of (a) the mineral greigite (Fe₅NiS₈), with various active centers (cuboids) of metalloproteins such as: (b) the thiocubane [Fe₄S₄] unit in protoferredoxins and ferredoxins; (c and d) the iron-nickel cuboidal C clusters of CO dehydrogenases which can reduce CO₂ to CO + H₂O; (e) the iron-nickel cuboidal A cluster of CO dehydrogenase which reacts CO with CH₃-Co(III)CoFeSP to make acetate; and (f) the twinned center to nitrogenase, the FeMn cofactor, in which N₂ is reduced (Einsle et al. 2002). Greigite may have acted as a primitive hydrogenase (as well as a CO dehydrogenase) by absorbing H₂ within the cuboids. Here, we suggest, it lost an electron to iron and a proton to sulfur (eq. 8), leaving a highly reactive hydrogen atom (H•), two of which can be used to reduce CO₂ to CO, a reaction that could be catalyzed at the nickel site (cf. Menon and Ragsdale, 2000). Affine sulfur sublattices, cubic close-packed in greigite, are distorted in the metalloenzyme centers. The relative concentrations of Fe³⁺/²⁺, Mo, Ni, and organic ligands (R and RS⁻) may dictate which of these entities formed in the first cells. Compiled from Russell et al. (1994, 1998), Russell and Hall (1997), Dobbeck et al. (2001), Drennan et al. (2001), Doukov et al. (2002), Einsle et al. (2002), Darnault et al. (2003), Svetlitchnyi et al. (2004), and Russell and Martin (2004).]
We assume that when the partial pressure of hydrothermal H₂ was locally high in the mound, it became adsorbed onto, or absorbed into, the Fe₄S₄ cubane of greigite where it lost its integrity (cf. nitrogenase, Fig. 7f; Einsle et al., 2002). Here it disassembled to a proton which attached itself to one of the sulfur atoms and an electron which was transferred to the de-localized electron cloud around the iron atoms, to leave a highly reactive hydrogen atom (H•), much as it does in metallic iron and the ferredoxin proteins (Kjekshus et al., 1972; Cammack, 1996; Morita, 2000; Fig. 7a):

\[ \text{H}_2 \rightarrow \text{H}\cdot + \text{H}^+ + e^- \]  

Activated thus, the hydrogen could attack the carbon dioxide (or bicarbonate), reducing it to CO and H₂O (Fig. 7a). In turn, reaction of the CO with methane thiol (CH₃SH) (Heinen and Lวางers, 1996) produced either deeper within the mound or in the crust below, generated the acetate (Huber and Wächtershäuser 1997; Schulte and Rogers, 2004; Russell and Martin 2004; Figs. 4, 7e; eqs. 9–11):

\[ 2\text{H}\cdot + \text{CO}_2 \rightarrow \text{CO} + \text{H}_2\text{O}, \]  

\[ \text{CO} + 2\text{CH}_3\text{SH} \rightarrow \text{CH}_3\text{CO(SCH}_3\text{)} + \text{H}_2\text{S}, \]  

and

\[ \text{CH}_3\text{CO(SCH}_3\text{)} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{CH}_3\text{SH}. \]

The CH₃SH can also modulate the activity of the metallic sulfide catalysts, converting them into active sites with spatial arrangements comparable to enzymes. For example, we assume that clusters of a greigite quarter cell Ni-2S-[Fe₄S₄]+ or Fe-2S-[NiFe₃S₄]²⁺ were sequestered by the CH₃S⁻ to produce SNiSFe₄S₄(CH₃S)₄ or SFeSnFe₄S₄(CH₃S)₄ in a process similar to that demonstrated by Bonomi et al. (1985). The sequestered active clusters would have been protected from dissolution on the one hand and from nucleation to nanocrysts on the other. The system was now primed for the organic takeover.

**Polymerization**

Whereas the simple amino acids and other modular organic compounds could have been produced by the reduction of CO₂ with hydrothermal NH₃, H₂, and CH₃S⁻, their polymerization to a peptide required a surface, perhaps provided by mackinawite or clay (cf. Ferris et al., 1996). We speculate that peptides were first condensed from amino acids (RCHNH₂COOH; R = organic ligand) via the loss of O or S from the carboxyl (-COO⁻) or thiocarboxyl (-COS⁻) group, and of 2H from an amine group (-NH₃) to form a peptide bond (-NCHOC⁻). The formation of a peptide bond may have alternated with lysine (NH₃·CH·COO⁻) and other amino acids have properties that particularly lend themselves to an organic takeover of the FeS membrane. Because of their relatively flexible structures, and because they inhibited crystallization and dissolution, these organic polymers, particularly the peptides, would have been superior to iron sulfide membranes in permitting growth and reproduction of cells (Milner-White and Russell, 2005). Depending on the numbers of different amino acids in a chain and their charge distribution, amino-acid polymers form helices, pleats, and other folds suitable as membrane constituents (Xu et al., 2001; Grosberg, 2002). The protonic potential drives organic polymerization via the regeneration of pyrophosphate. Concentrated within the pores and on mineral surfaces and subject to oscillating pH and Eh, other organic monomers are also assumed to have reacted through condensation to form sugars and nucleic acids (Russell et al., 2003; Table 1).

**Organic takeover of the membrane**

Protolife, as the evolving organic by-product of reactions in the mound (eq 7), continued to develop as more organic molecules were produced and became involved in feedback cycles (i.e., cycles that repeated production of molecules such as peptides and RNA). Under hydrodynamic pressure, initially peptides and other polymers would have coated the inside of the FeS cavities and plugged the pores, lowering permeability and increasing electrical resistance across the membranes. Eventually such organic molecules would have replaced the FeS membranes altogether. Because of their relatively flexible structures, and because they inhibited crystallization and dissolution, these organic polymers, particularly the peptides, would have been superior to iron sulfide membranes in permitting growth and reproduction of cells (Milner-White and Russell, 2005). Depending on the numbers of different amino acids in a chain and their charge distribution, amino-acid polymers form helices, pleats, and other folds suitable as membrane constituents (Xu et al., 2001; Grosberg, 2002).

Polymers (proteinoids) in which glycine (NH₃·CH₂·COO⁻) alternates with lysine (NH₃·CH₂·(CH₃)·NH·CH·COO⁻) and other amino acids have properties that particularly lend themselves to an organic takeover of the FeS membrane. Microspheres do form from lysine-rich proteinoid in seawater both on heating and when made alkaline, perhaps by charge neutralization and the initiation of hydrophobic bonding (Fox et al., 1962; Rohlfing, 1975). But such a hydrophobic membrane would still have needed to house [Fe₄S₄] electron transfer sites (Tabushi et al., 1988), and structures such as Ni-S₂-[Fe₄S₄]-S₂-Fe to catalyze the reaction between CO₂ and H₂.

An optimal 25 percent yield of pyrophosphate was achieved only between 38° and 51°C:

\[ \text{HPO}_4^{2-} + \text{CH}_3\text{COPO}_4^{2-} \rightarrow \text{HP}_2\text{O}_7^{2-} + \text{CH}_3\text{COO}^- \]  

Attached to a mineral surface, the resulting pyrophosphate can, in theory, extract the constituents of water from the opposite ends of main-chain amino acids and so condense or polymerize them as the carbon and nitrogen atoms are bonded:

\[ \text{NCH}_2\text{COO}^- + \text{HPO}_4^{2-} + \text{NCH}_2\text{COO}^- \rightarrow \text{NCH}_2\text{CONHCH}_2\text{COO}^- + 2\text{HPO}_4^{2-} + \text{H}^+ \]  

Protons driven through the membrane by the protonmotive force may have recharged the phosphate (Josse, 1966; Baltscheffsky, 1996; Russell and Hall, 2002; Table 1, Figs. 6b, 8):

\[ 2\text{HPO}_4^{2-} + \text{H}^+ \rightarrow \text{HP}_2\text{O}_7^{2-} + \text{H}_2\text{O} \]
and CO and CH₃S⁻. The amide links within the membrane that constitute the peptide chains carry a small positive charge. About five of them in a chain could have bonded with NiS₂Fe₄S₄(CH₃S)O₄²⁻ and Fe₄S₄(RS)O₄²⁻/³⁻ clusters to generate an organometallic complex in the form of a protective nest. However, for a nest to be effective amino-acid monomers had to be of an alternating stereochemistry (i.e., with left- and right-handed, L and D, amino acids alternating), unless it included a substantial proportion of glycine residues, the only biological amino acid to have no preferred stereochemistry (Milner-White and Russell, 2005; Fig. 9a). Nests depend on the fact that the main-chain amine groups in peptides act as delta positive sites (i.e., have a relative +ve charge).

The inorganic diphosphate HP₂O₇³⁻, or the organic adenosine triphosphate (ATP²⁻) required for energy storage within the membrane could be nested in the same way (Milner-White and Russell, 2005; Fig. 9b). Sequestered thus, both the FeS clusters and the phosphates could act more efficiently as
energy transfer stores. Thus, the presence of achiral amino acids, normally considered a major obstacle in the explanation of life’s emergence (Cairns-Smith, 1982), would be a positive advantage to the sequestering of iron(nickel) sulfides and inorganic phosphates.

Crude coding of the peptides

In our model volcanically derived pyrophosphate would have contributed to organophosphates such as RNA monomers generated in the hydrothermal mound that in turn would have adhered to metal-rich mackinawite or other layered minerals in the membrane (Russell and Hall, 1997, 2002; Bebbie et al., 1998, their Fig. 5a; Rickard et al., 2001). If they did, then the side chains (i.e., the nitrogen bases of the RNA molecules) could have presented clefts or openings, each comprised of three RNA monomers that would have adhered, harbored, and gripped a side chain of various amino acids, as demonstrated in Figure 10 (Mellersh, 1993). In other words, affinities between these clefts (i.e., the codons) with amino acids would have acted not only as a way of presenting the amino group (-NH$_3^+$) to the carboxyl (-COO$^-$) of another, so facilitating their polymerization, but they would also have influenced which of the ten or so “abiotic” amino acids were involved in the eventual sequence (Woese, 1967; Russell et al., 2003). Amino acids with hydrophobic side chains showed particular affinity for clefts in which the nitrogen base uracil was the central nucleotide, while those with hydrophilic side chains were favored by those triplets where adenine or guanine were the bases that held the middle site (Konecny et al., 1995). Thus a rather crude coding would have been effected. For example, the nucleic acid polymer, polyadenosine, would have coded for the side chains of the amino-acid lysine (-CH$_2$$_2$·NH$_3^+$) to produce polylysine (-NH$_2$·CH$_2$$_2$·CH(NH$_2$)-CO$_2$H, as it does today, although through a more complex pathway (Mellersh and Wilkinson, 2000). With its positively charged side chains, polylysine could then have taken over from mackinawite as a surface to attract phosphates, promoted polymerization of further RNA, and thereby have facilitated the production of more peptide chains—chains that could also have contributed to the emerging organic membrane.

In the absence of amino acids the RNA may have reproduced RNA strands through hydrogen bonds, although with sequences of the opposite sense, by what is known as base pairing (Poole et al., 1999). These “antisense” strands would then have coded for amino acids with contrasting properties (e.g., for hydrophobic varieties like the side chain of methionine (-CH$_2$$_2$·SH.CH$_3$) demonstrated in Figure 10 as opposed to the hydrophilic side chains of amino acids such as lysine; Konecny et al., 1995). 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 microwatties in the 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.

Crudely coded amino-acid sequences that proved useful in reproducing RNA, or that improved membrane function, would have survived, as would their RNA. Once RNA templates for useful amino-acid sequences were passed on to daughter cells, then evolution had begun (Baymann et al., 2003; Russell et al., 2003). We can think of these interactions and the dissemination of peptides back to the fluid within
compartments mineralogically as constituting unsuccessful attempts to create oscillating zones on transient mineral surfaces.

Evolutionary Assays in the Hydrothermal Mound

The first reproducing and replicating cells would not be viable without the constant hydrothermal feed, syntrophic cooperation with their neighbors, and the protection provided by the mound. Any individual cells entrained in the hydrothermal flow and dispersed to the ocean would die. Indeed, Martin and Russell (2003) argued that evolution in the mound continued right up to the differentiation of the two unicellular domains of life, the bacteria and the archaea (Koga et al., 1998). That there is a sufficient time span for the emergence and early evolution of life in such a mound has been demonstrated by Früh-Green et al. (2003), a finding that counters a criticism of hydrothermal theories mounted by Bada (2004). In the earliest stages of evolution, genes were shared, swapped, and transferred by mobile DNA as well as by protoviruses. All life may have evolved from a community of cells—a community constituting the “last universal common ancestor” (the LUCA of Woese et al., 1990; Stetter, 1996) or, more accurately, the “last common community” (the LCC of Woese, 1998; Macalady and Banfield, 2003; Fig. 11).

In the protective environment of the mound what would be the first evolutionary steps? As J. D. Bernal (1960, p. 34) has remarked, “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.” It was the organic detritus and waste of the first autotrophic or lithotrophic cellular communities that provided both the fuel and the material for organotrophic life. Put another way, the remains of the first lithotrophs constituted a secondary source of electrons and nutrient. Organotrophic metabolism also requires respiration (i.e., the oxidation of organic molecules by electron acceptors to release energy), and the biochemical evidence suggests that photolytic MnIV and S0 joined FeIII as electron sinks accessible to unicellular microbes while still within the mound (Stetter and Gaag, 1983; Myers and Nealson, 1988; McFadden and Shiv-Jyoty, 1991; Pace, 1997; Russell and Hall, 1997; Reysenbach and Lovley, 2002; Fig. 12).

The process of reduction of MnIV is similar to that of FeIII and provides comparable energy. But elemental sulfur is a nonmetal and is less easily reduced, and its reduction provides less energy (Fig. 12). Nevertheless, the means to reduce sulfur had been perfected before the emergence of the last universal common ancestor, i.e., when life was still restricted to the mound. S0 is insoluble but polysulfide (S8), one of the products of SO2 photolysis, is the substrate of sulfur respiration (Schauder and Kröger, 1993). Significant quantities of S8 would have rained into the early ocean from the atmosphere (Farquhar et al., 2001; Mojzsis et al., 2003).

The beginning of Darwinian evolution

Cells in the mound could have developed a variety of ways to gain energy and synthesize organic molecules suitable for their requirements. Genes to synthesize organic molecules appropriate to the various and oscillating conditions near the mound’s surface would be shared at first. In time, however, pressure would build for cellular metabolisms, and thereby
the genes, to specialize so they might exploit different although overlapping conditions. Differentiation took place into groups capable of growing deeper in the mound where temperature was relatively high although chemical gradients were low. We suggest that this differentiation was what led to the rapidly evolving precursors of the bacteria, the homoaacetogens, initially suited to low to moderate temperatures, and the archaea, the methanogens, initially suited to higher temperatures. The homoaacetogens gained, and continue to gain, their energy by the overall reaction:

$$4H_2 + H^+ + 2HCO_3^- \rightarrow CH_3COOH^- + 4H_2O. \quad (15)$$

The first methanogens gained the extra energy available in reduction all the way to methane, using some of the same enzymes (Shock et al., 1998; Amend and Shock, 2001). However, a special complex tungstoenzyme and a vitamin operating at very low redox also were required to facilitate the high-temperature reaction (Adams, 1998; Thaer, 1998):

$$4H_2 + H^+ + HCO_3^- \rightarrow CH_4 + 3H_2O. \quad (16)$$

Another opportunity open to the precursors of the methanogenic archaea was the use of acetate waste from proximal acetogens (the aceticlastic methanogens):

$$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^- \quad (17)$$

**Life Away from the Mound**

Because the first cells would have found the Hadean ocean to be a nutritional desert, prone to tempestuous conditions and to wildly fluctuating temperatures brought about by meteorite impacts and dust clouds (e.g., Bjerrum and Canfield, 2002), it seems likely that the mesophilic and thermophilic acetogens, methanogens, and organotrophs (precursors of the bacteria and the archaea) occupied and migrated from near the base of the mound across and beneath the ocean floor where they could have maintained their reliance on mineral surfaces, the cooperative degradation of otherwise indigestible substrates in syntrophic interactions, and the supply of $H_2$ emanating through the oceanic crust. Thus the deep biosphere was inaugurated (Parkes et al., 1990, 1994; Thorseth et al., 1995; Wellsbury et al., 1997). Even today it is estimated that 40 times more prokaryote cells live in the subsurface than in the oceans (Whitten et al., 1998).

Obduction of a portion of the deep biosphere eventually brought some bacteria into an exhalative “manganiferous photic zone.” Here they evolved to exploit solar energy, eventually managing to use the hydrogen in water and emitting oxygen as waste. Free-living oxygenic photobacteria could then have colonized the ocean surface and begun the process of precipitating the banded iron formations, probably by 3.7 Ga (Dymek and Klein, 1988; Rosing, 2002). But this model of iron formation must have been in place by the beginning of the geologic record (Pace, 2002). It was the oxidation of the ferrous iron in the oceans and of atmospheric methane produced by the methanogens that prevented the build-up of oxygen in the atmosphere before about 2.4 Ga (Lécyuyer and Ricard, 1999; Catling et al., 2001; Kasting, 2001; Bjerrum and Canfield, 2002).

**Tests and Expectations**

If the steps toward the emergence of life were as we have suggested, a series of predictions must follow. Central to our hypothesis is that the hydrothermal mound acted as a natural self-restoring flow reactor and that the emergence of life there was rapid. Knowing or surmising the physicochemical conditions under which the hydrothermal mound was generated and sustained, experimental organic synthesis experiments should be carried out in a series of microreactors duplicating the pressure, temperature, redox, and pH conditions outlined in the text. Experiments in these reactors should demonstrate: (1) acetic acid synthesis, (2) amino-acid synthesis, (3) peptide synthesis, (4) nest conformation induced in achiral peptides by [(Fe$_2$Se$_3$[4RS])$^{+2}$] and HP$_2$O$_7^{2-}$, and (5) surface-bound RNA codon/amino-acid affinities.

Because mineral exploration has focused on Cyprus, Besshi, and volcanogenic massive sulfide (VMS) deposits of high-temperature origin, hydrothermal mounds generated at ancient alkaline springs and seepages of moderate temperature are likely to have gone unremarked. In the acidulous Hadean and early Archean oceans any primary carbonate would have been rapidly dissolved to leave a disorganized rubble of chert, sulfides, oxides, hydroxides, and clays difficult to recognize for what it was. Nevertheless, we might expect that any such surviving rubble will preserve vestiges of once hollow structures in both chert and sulfide similar to those found at the Tynagh Pb-Zn deposit. Such structures might be found in ancient hydrothermal cherts and fossil sinter (Russell, 1988; Garcia-Ruiz et al., 2003).

**Conclusions**

Life emerged as a channel for the transformation of chemical and physical energy and materials juxtaposed on the submarine surface of the early Earth by catalyzing reactions between CO$_2$ and H$_2$. Tributaries to the channel comprised the alkaline hydrothermal fluids of moderate temperature that contained $H_2$, HS$^-$, CH$_3$S$^-$, NH$_3$, Mg$^{2+}$, and trace amounts of CN$^-$. The remaining contribution was the CO$_2$ and HP$_2$O$_7^{2-}$, as well as Fe$^{2+}$ and FeOOH and other transition elements, from the acidulous Hadean ocean. We argue that reactions between these components took place where thermal and chemical gradients were high, in a hydrothermal mound that acted as a self-restoring natural flow reactor. In this mound inorganic bubbles or microcavities defined by nanocrystals of iron compounds, chiefly of Fe(Ni)$_8$, but including phosphate and oxyhydroxide, acted as catalytic chambers for the synthesis of organic molecules. These compartments were open to reduced components at their base and selectively permeable and semiconducting at their upper surface. They would have expanded, budded, and multiplied as hydrothermal waters were injected from below. Acetate and water, the main products of the reaction of $H_2$ with CO$_2$, were eluted to the ocean. However, a proportion of the organic by-products were retained in the pores. Concentrated thus, they interacted to produce amino acids, peptides, and protometalloenzymes. The metalloenzymes improved the catalytic efficiency of the
budding system. Minor concentrations of RNA, adhering to mineral surfaces, brought some order to the structure of peptides and also enabled the transfer of genetic information to budding protocells and their evermore organic progeny. Once this happened evolution would ensue.

Most of the time, the sulfur concentrations at an alkaline seepage would have been too low to give anything but the flimsiest of barriers between the hydrothermal and ocean waters. Even when a barrier did form, the internal structure of a mound may have been more particulate and dendritic than compartmentalized. However, given that thousands of alkaline seepages, each covering hundreds of square meters, would have operated for millions of years on the early Earth, we consider it to be inevitable that organic interactions of the type described here occurred in many of the submarine hydrothermal mounds. Bacteria have flourished around hot springs ever since and, in some cases, have been responsible for the deposition of large sulfide deposits at or just below the sea floor (Boyce et al., 1983, 2003; McGoldrick, 1999; Rasmussen, 2000; Fellick et al., 2001).

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