

100th Anniversary Special Paper: On Hydrothermal Convection Systems and the Emergence of Life

MICHAEL J. RUSSELL,[†] ALLAN J. HALL, ADRIAN J. BOYCE, AND ANTHONY E. FALICK

Scottish Universities Environmental Research Centre, Rankine Avenue, East Kilbride, Glasgow G75 0QF, Scotland

Abstract

Not only have submarine hydrothermal systems been responsible for a variety of mineral deposits, they may also have contributed to the emergence of life in the Hadean. Sulfide deposits can be precipitated where metal-bearing hydrothermal solutions invade bacteriogenic H₂S-bearing wet sediments and the overlying seawater or brine. Similarly, life might be viewed as a complex organic product that emerged when and where hydrothermal H₂ and other reduced chemical species reacted with CO₂ and other mildly oxidized molecules dissolved in the Hadean ocean. Semipermeable and semiconducting FeS barriers or membranes would have precipitated spontaneously where H₂ and HS⁻-bearing alkaline waters at $\leq 110^{\circ}\text{C}$ seeped into the cool mildly acidic Fe-bearing Hadean ocean at a submarine hydrothermal mound on a ridge flank or on the deep ocean floor. The mound, consisting of Mg-rich clays, ephemeral carbonates, green rust, as well as the sulfides, acted as a natural, self-restoring hydrothermal reactor. In particular, the sulfide barriers, composed of mackinawite and greigite, prevented the immediate titration of the two fluids and controlled their interactions. Metal sulfides were, and in tiny amounts are still, vital to all cells. Among other reactions they help catalyze the reduction of CO₂ in autotrophic bacteria, including photosynthetic organisms. And the structure of greigite (NiFe₈S₈) is remarkably similar to the active sites (e.g., NiFe₄S₅) of the enzyme promoting the early metabolic pathway that generates acetate (CH₃COO⁻) and H₂O from CO₂, H₂, and a methyl group (-CH₃). So clusters of greigite, sequestered in a simple organic envelope, could have acted as a protoenzyme, catalyzing the synthesis of acetate in the hydrothermal mound in the same way.

Although, like "spent" ore fluid, most of the acetate and all of the water would have been lost to the Hadean ocean, an acetate fraction retained in microcavities within the mound could have combined to form the simple organic building blocks of life. Hydrothermal ammonia and minor cyanide also would have contributed to the synthesis of amino and nucleic acids. Traces of phosphorylated organic molecules, such as RNA (ribonucleic acid), would have adhered to mineral surfaces in the membranous barriers. Once their phosphates were bonded to such a surface, short RNA strands could have polymerized and provided a crude code for the assembly of variable sequences of amino acids (incipient proteins) generated in the same milieu. Alternatively, they could have replicated further RNA. Amino-acid sequences were a significant component of the first membranes and would have influenced membrane and cell survival. Once RNA codes for successful amino-acid sequences were passed on to daughter cells then life could be said to have emerged and evolution to have begun. Bacteria have flourished around hot springs ever since and on occasion have been responsible for the deposition of giant base metal sulfide deposits at or below the sea floor.

Hence the study of life may be best begun by the study of those physico-chemical phenomena which result from the contact of two different liquids.

Stéphane Leduc 1911, p. xiv.

Introduction

LEDUC'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

[†] Corresponding author: e-mail, michaelr@chem.gla.ac.uk

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., $[C_{70}H_{129}O_{65}N_{10}P(Fe,Ni,Co,Zn,Mo)S]$ (cf. Redfield et al., 1963; Orr, 1978; Morel and Hudson, 1985; Faggebakke 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 membranes, 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 hydromagnesite 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_3S^- ; Heinen and Lauwers, 1996), acetate (CH_3COO^- ; 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

Standard biochemical terms	Definition	Notes
Activated hydrogen Anhydride bond ADP	A short-lived, highly reactive state of hydrogen A bond formed by the elimination of the constituents of water The energy-depleted molecule, Adenosine DiPhosphate	Consists of hydrogen atom with a single electron e.g., a pyrophosphate bond ADP needs chemical energy (via metabolic processes) to return to ATP
Amino acid	A molecule with general formula $\text{NH}_2\text{-CHR-COOH}$, where "R" is a side chain	The side chain influences the properties of the amino acid
ATP	The energy-rich molecule, Adenosine TriPhosphate, consisting of the nucleic acid base, adenosine, and 3 consecutive phosphate groups	ATP can drive a multitude of biochemical reactions, e.g., polymerizations by the removal of the constituents of H_2O
Chirality	The noncongruence of molecules with their mirror image	Conventionally such molecules are termed either left or right handed
DNA	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	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
Enzyme	A large protein molecule which catalyses one or more biochemical reactions	The overall shape of an enzyme partly controls its catalytic properties; metallic cations bonded within proteins often also influence their biochemical role
Ferredoxin	An enzyme that contains an iron-sulfur ionic center	The variable valence states of iron contribute to the electrochemical and/or biochemical role of ferredoxins
Heterochiral	Of mixed chirality	Polymers may be heterochiral
Heterotroph (or organotroph)	An organism requiring a source of organic carbon for biosynthesis	
Lithotroph (or autotroph)	An organism that uses CO_2 as its sole source of organic carbon, and other simple inorganic constituents such as hydrogen, ammonia and inorganic phosphate	
Monomer	A single molecule that contributes to a molecular chain (polymer)	e.g., RNA monomers
NAD	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)	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
Nucleic acid bases	The five bases (ring structures of C, N, H, O) are adenine (A), thymine (T), guanine (G), cytosine (C), and Uracil (U)	ATGC only occur in DNA and AUGC only in RNA
Nucleotide	An individual nucleic acid comprising a nitrogenous ringed base, a ribose or deoxyribose sugar, and a phosphate	
Organophosphates	A general term for organic molecules which contain P usually within a phosphate group (PO_4) ³⁻	
Peptide (strictly polypeptide)	A chain of amino acids linked by peptide bonds which are also known as amide bonds	The peptide bond results when amino ($-\text{NH}_2$) and carboxyl ($-\text{COOH}$) groups of two amino acids react by extraction of the constituents of a water molecule
Protein	Proteins are long chains made from an inventory of 20 amino acids in current living systems	The "sequence" of amino acids characterizes a protein and controls its biochemical role
Protonmotive force (pmf)	Protons moving downgradient through the membrane can do work	The pmf drives the formation of "high-energy" bonds between phosphate to produce pyrophosphate (cf. chemiosmosis)
Racemic	A mixture of a particular chiral molecule in which the left- and right-handed varieties are in equal proportion	
RNA	RiboNucleicAcid has the same style of structure as DNA	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
Siderophore	A ligand with a high affinity for Fe^{III} attached to a short heterochiral chain of amino acids	Produced by bacteria to acquire iron
Sugars	Compounds that contain only carbon, hydrogen, and oxygen, usually in a ring structure of 5 or 6 carbons	Glucose is a 6C-ring sugar ($\text{C}_6\text{H}_{12}\text{O}_6$) and is an important energy reservoir for metabolism because of high energy C-C bonds. Ribose and Deoxyribose have 5C ring structures
Syntrophy	The collaboration of organisms in degrading a substrate that is otherwise resistant	
Emergence of life terms and/or phrases	Explanation	
Acidulous	Mildly acidic	
Autogenesis or abiogenesis	Originating from inorganic molecules	
Emergence of life	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	
Onset of life	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)	
Plasmogenesis	Originating from preformed organic molecules, such as proteins and lipids suspended in an aqueous fluid	
Primitive polymerase	A catalyst of polymerization	
Protoferredoxin	A chemical imagined to exist as a precursor before modern biosynthesized ferredoxins	
RNA instructors	Sequences of RNA that control the molecular sequence of the amino acids comprising a peptide	
Thermophoresis	The movement of particles (e.g., DNA) against a temperature gradient from hot to cold	
Useful amino-acid sequences	Sequences of amino acids that enhance catalytic efficiency	

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 autogenic 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 unaddressed (e.g., Nilson, 2002; cf. Cody, 2004). Bada (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 $\leq 20^{\circ}\text{C}$ (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 H_2 , CO_2 , SO_2 , P_4O_{10} , and N_2 degassed through volcanoes or introduced by micrometeorites and comets were trapped gravitationally to comprise the volatilesphere (Goldschmidt, 1952; Yamagata et al., 1991). Any reduced gases, such as CO , CH_4 , and H_2S , were rapidly oxidized by the hydroxyl radical generated by the photolysis of water vapor in atmosphere (Kasting, 1993; Kelley and Fröh-Green, 1999; Scott et al., 2004). The partial pressure of CO_2 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; Ricardo 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.

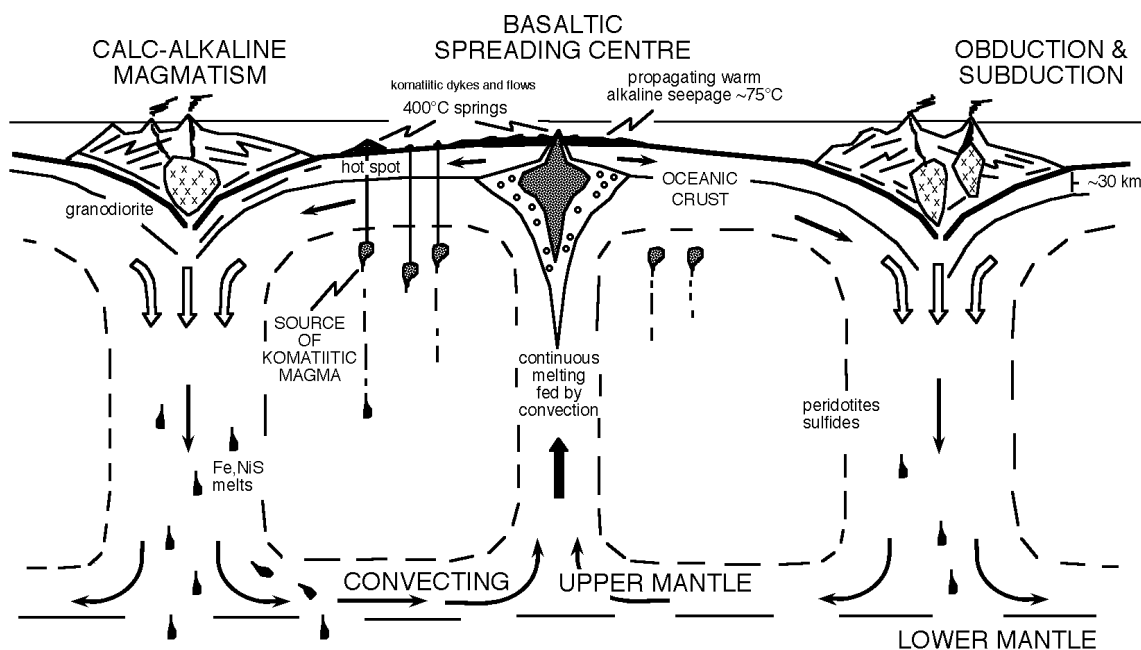


FIG. 1. Cross section of a mantle convection cell for the Earth at >4 Ga (Davies, 1992; Shock, 1992; Russell et al., 2003). Chemosynthetic life may have emerged at a warm alkaline seepage and expanded into the surrounding sediments and crust. The transition elements catalyzing the reduction of CO_2 in 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.

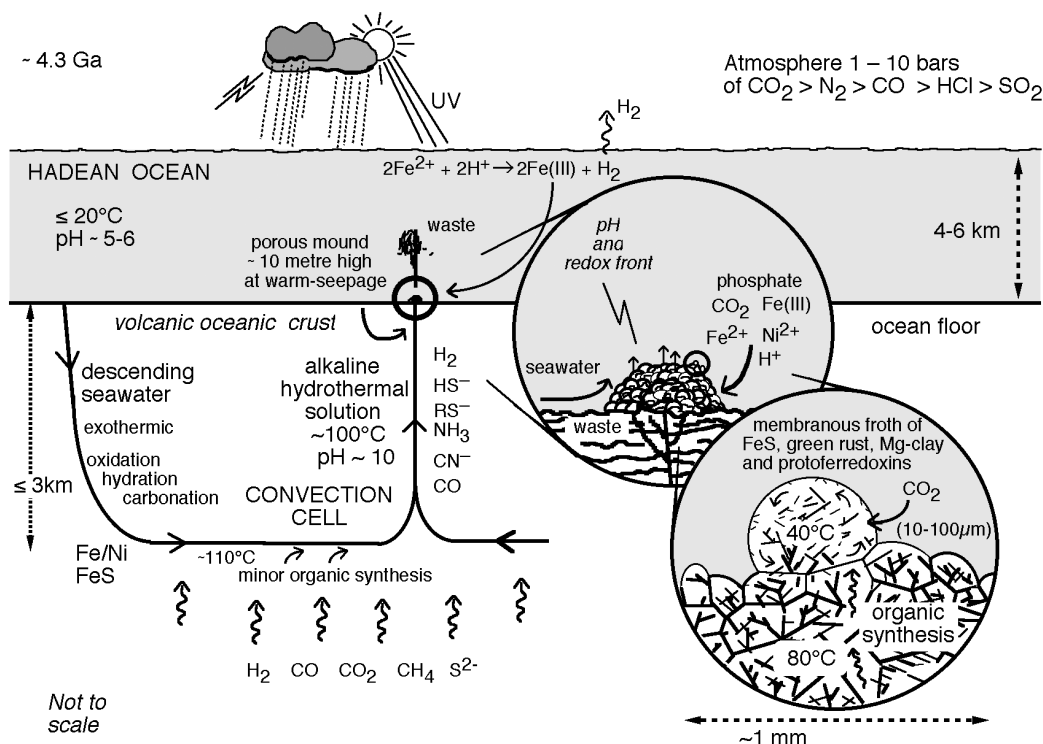
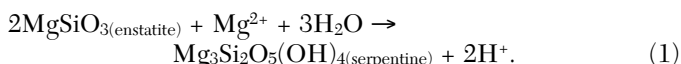


FIG. 2. Model environment for the emergence of life at a submarine seepage on the ocean floor (Russell and Hall, 1997; Russell and Martin, 2004). Here, a hydrothermal mound (see insets) acted as a self-restoring flow reactor and fractionation column. In it hydrothermal hydrogen and ammonia reacted with 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 ($\geq 350^\circ\text{C}$) 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 solutions, then as now, were rendered acidic (pH ~ 3) as ocean water in the downflow, serpentinized mafic rock at high temperature (Seyfried and Bischoff, 1981; Douville et al., 2002):



Acidic solutions can dissolve transition and base metals from sulfides and silicates comprising the crust (Von Damm, 2000; Douville 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 basalt, as in present-day systems, to produce magnesium hydroxide sulfate hydrate, further contributing to the low pH of high-temperature hydrothermal solutions (Bischoff and Seyfried, 1978; Janecky and Seyfried, 1983):

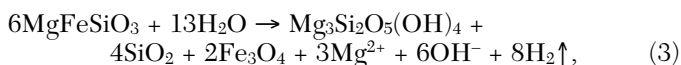


The Rainbow hydrothermal system operating in ultramafic rocks, although at the slow-spreading mid-Atlantic Ridge at 36°N , probably offers the best modern geochemical analog for Hadean high-temperature hydrothermal fluids because the geochemical and mineralogical composition of its source rock is similar to that of the Hadean ocean crust (Holm and Charlou, 2001; Douville et al., 2002). Here, iron concentrations are 24 mM/L.

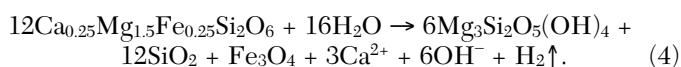
Minor to trace quantities of other bioessential elements, such as Mn, Zn, Ni, Co, Mo, Se, W, and P, also would have been delivered to the Hadean ocean in these hot springs (Goldschmidt, 1937; Von Damm, 1990; Kakegawa et al., 2002). Similar high-temperature convection cells would have developed at sites of meteoritic impact, over mantle plumes, and at destructive plate margins (Whitehead et al., 1990; Ames et al., 1998; Barrie et al., 2001; Byerly et al., 2002). Despite the high metal sulfide contents of these hot springs there would have been relatively little precipitation on cooling and exhalation, for although supersaturated, in the absence of a neutralizing alkaline ocean and the lack of anhydrite around the vents, much of the metal sulfide would have passed directly into the acidulous ocean.

Low-temperature systems ($85^\circ\text{--}115^\circ\text{C}$) in ultramafic hosts

Subject to strong tectonic and tidal stress exerted by the close and rapidly orbiting moon (Gaffey, 1997; Davis and Becker, 1999), the ocean crust of the ridge flanks, floor, and trenches would have fractured and thereby permitted ocean 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 serpentinization and oxidation of orthopyroxene at these low temperatures would have produced silica and magnetite with the release of H_2 and OH^- :



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):



Such serpentinization would have increased markedly at around 85°C (Wenner and Taylor, 1971; Macleod et al., 1994; Lowell and Rona, 2002). The increase of rock volume brought about by serpentinization may have closed fractures at about 115°C in the absence of igneous intrusion (Wenner 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 (Krishnrao 1964) would have acted as reducing agents and catalysts for abiogenic production of millimolar quantities of CH_3S^- and NH_3 as well as micromolar quantities of CN^- (Shock and Schulte, 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 (Marteinson et al., 2001; Geytner et al., 2002).

Ocean Water, the Hot Spring Sink

In the absence of subaerial continents, Hadean ocean chemistry would have been dominated by atmospheric CO₂ 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 mM/l of Fe²⁺ 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 Fe²⁺ of windblown derivation in the carbonic lakes in Cameroon (pH ~5.5). Here Fe²⁺ concentrations are between 10 and 20 mM/l (Sigurdsson et al., 1987; Kling et al., 1989). Some of the Fe²⁺ 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 CO₂ 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—H₂ and NH₃ in hydrothermal solution, and CO₂ and HP₂O₇³⁻ 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 ~10, ~110°C) would have exhaled directly into the cool acidulous ocean (pH ~5.5, ~20°C; Russell et al., 1989; Shock, 1992; Macleod et al., 1994; Fig. 2). In time, reaction of hydrothermal hydroxyl (OH⁻) and hydrosulfide (HS⁻) with Fe²⁺ 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⁻) and the polar formaldehyde (H₂CO) would have been adsorbed in the mound and on FeS/Fe₃S₄ membranes and thereby retained (Leja, 1982; Rickard et al., 2001).

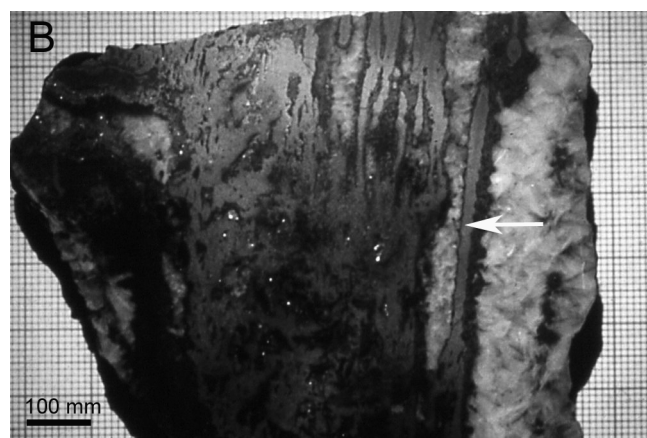
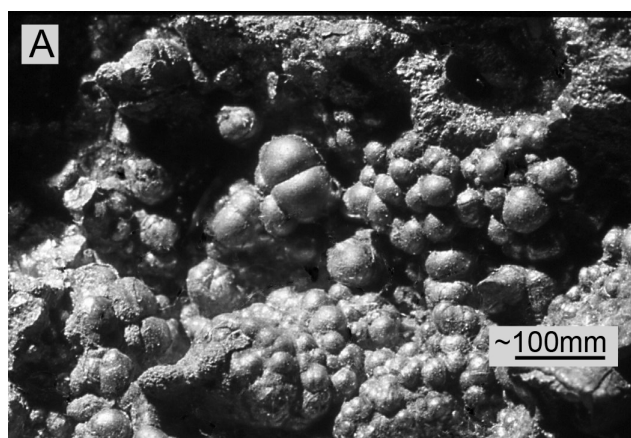


FIG. 3. a. Pyrite botryoids (bubbles) formed a surface at a 350 Ma warm spring feeding part of the Tynagh lead-zinc deposit, Ireland. b. A natural “chemical garden” (Russell, 1988) from Tynagh comprising pyrite spires (gray) embedded in coarse barite (white). The darker material surrounding the pyrite core (arrowed) is largely tennantite. Pyrite is presumed to have replaced iron monosulfide membranes in both cases (Banks, 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, FeS₂ (compare with Fig. 4).

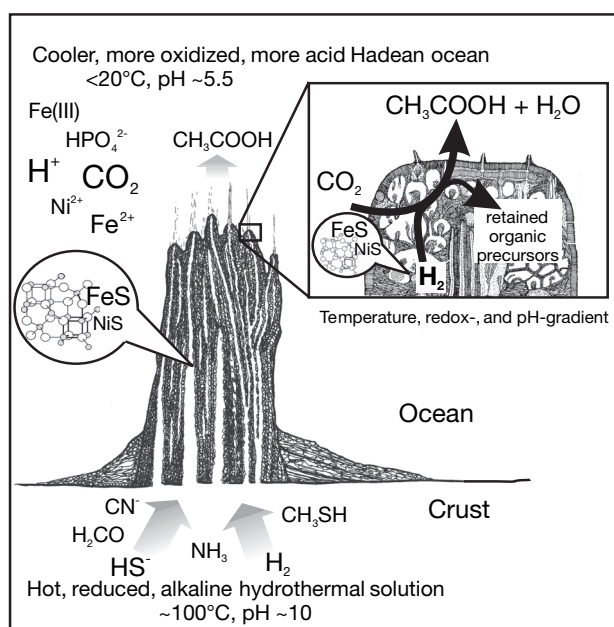


FIG. 4. The hydrothermal mound as an acetate generator. Note the ocean is cooler, more acidic, and more oxidized than the hydrothermal solution. Thus steep physicochemical gradients are focused at the margin of the mound. The detailed cross section of the surface (see inset) illustrates the sites where anionic organic molecules are produced, constrained, react, and automatically organize to emerge as protolife (from Russell and Martin, 2004, with permission). Compartmental pore space may have been partially filled with rapidly precipitated dendrites. The walls to the pores comprised nanocrystals of iron compounds, chiefly of FeS (Wolthers et al., 2003) but including vivianite and green rust. The pores and bubbles acted as catalytic culture chambers for organic synthesis, open to H_2 , NH_3 , and CH_3S^- at their base, selectively permeable and semiconducting at their upper surface. The font size of the chemical symbols gives a qualitative indication of the concentration of the reactants.

Formation of the first compartments

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 for HS^- (Seward and Barnes, 1997).

The conical mounds of Mg-rich clay, tens of meters high, forming at a submarine hydrothermal seepage in a fjord off the north coast of Iceland may be a modern analogue. Although these fluids do contain about 10 μM of HS^- , no sulfide precipitates are recorded (Geptner et al., 2002). Nevertheless, the conical mounds do offer the kind of porous

framework considered necessary for the synthesis of organic molecules (Geptner et al. 2002; Russell and Martin, 2004).

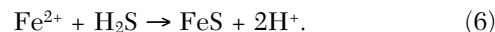
The Onset of Life

Organic syntheses

Shock (1990, 1992), Shock and Schulte (1998), and Amend and Shock (2001) have calculated the free energies of reaction for the production of methane (CH_4) and acetate ($H_3C\cdot COO^-$) as hydrothermal fluid mixes with mildly oxidized ocean water. Although the strongest thermodynamic drive is to the production of CH_4 as aqueous CO_2 reacts with hydrothermal H_2 , 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):

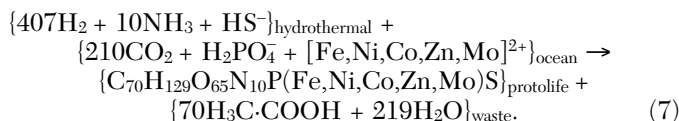


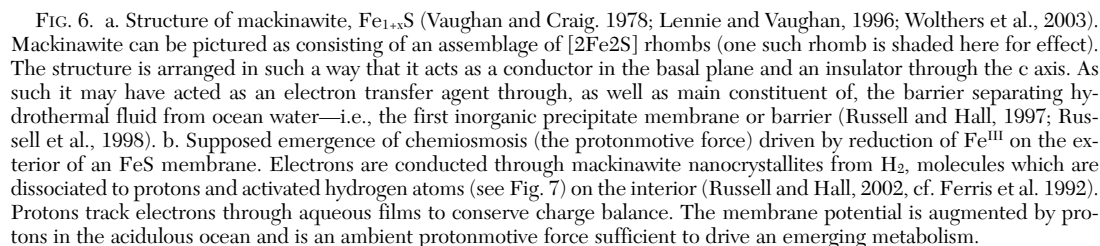
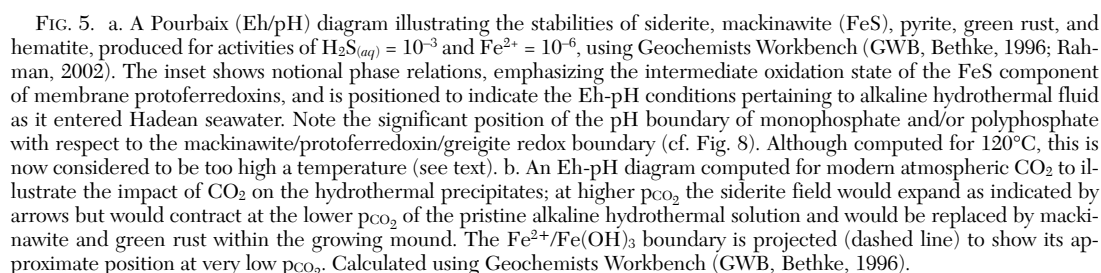
However, the acetate reaction is catalyzed in autotrophic living cells by metalloenzymes and vitamins (Thauer, 1998). Thus we might expect inorganic catalysts capable of promoting organic synthesis at the dawn of life to be comparable to the active centers of the metalloenzymes, i.e., sulfides of iron with ancillary nickel. As we have seen, such sulfides were a feature of hydrothermal mounds. Dissolved Fe^{2+} reacts with H_2S (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):



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 $[(FeNi,Co)_{1+x}S]$ and greigite $(NiFe_5S_8)$ membranes. The ~110°C alkaline hydrothermal fluid directly supplied the reduced chemical species such as HS^- and chemical energy, particularly H_2 , whereas the ocean supplied the transition metals such as Fe^{2+} derived from ~400°C springs, as well as protons and the oxidized species, CO_2 and $FeOOH$ (Fig. 6b). The natural catalytic reactor provided just the 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 ($NH_3^+\cdot CH_2\cdot COO^-$; Hennessey et al., 1992), and a much smaller proportion of nucleic acids. The reaction that produces waste acetate ($H_3C\cdot COO^-$), water, and the organic molecules that constituted a protolife can be summarized notionally as:





This C_{70} 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 homoacetogens—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 nanocrystals that comprised the walls to the microcavities in our model acted as the catalytic surfaces for CO_2 reduction and acetate formation (Figs. 6, 7a). The structure of greigite (as $Ni-S_2-[Fe_4S_4]-S_2-Fe$) (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 CO_2 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 $NiFe_4S_5$ within the protein (Fig. 7c-e). The Fe_4S_4 clusters of greigite are assembled from Fe_2S_2 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).

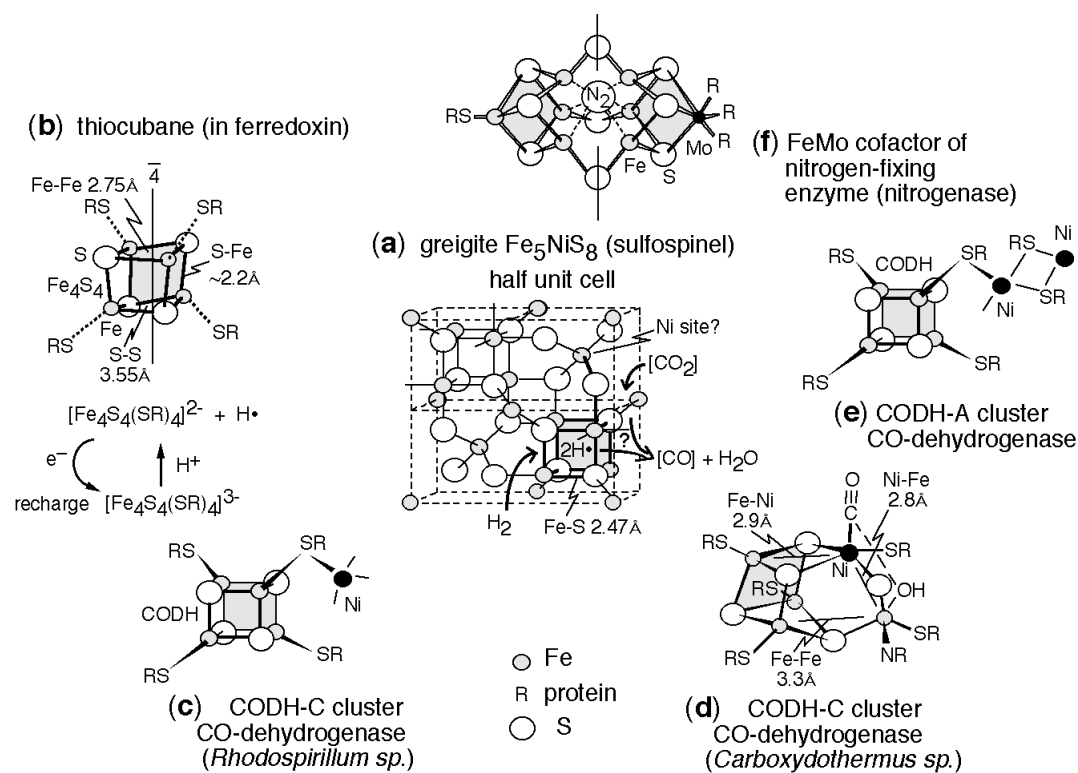
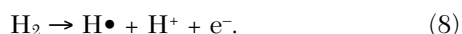
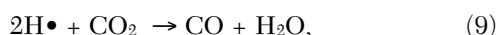


FIG. 7. Structural relatedness (emphasized by shading of the $2Fe_2S$ rhomb component) of (a) the mineral greigite (Fe_5NiS_8), with various active centers (cuboids) of metalloproteins such as: (b) the thiocubane $[Fe_4S_4]$ unit in protoferredoxins and ferredoxins; (c and d) the iron-nickel cuboidal C clusters of CO dehydrogenases which can reduce CO_2 to $CO + H_2O$; (e) the iron-nickel cuboidal A cluster of CO dehydrogenase which reacts CO with $CH_3-Co(III)CoFeSP$ to make acetate; and (f) the twinned center to nitrogenase, the FeMo cofactor, in which N_2 is reduced (Einsle et al. 2002). Greigite may have acted as a primitive hydrogenase (as well as a CO dehydrogenase) by absorbing H_2 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 ($H^\bullet$), two of which can be used to reduce CO_2 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 $Fe^{3+/2+}$, 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).

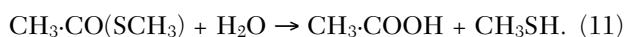
We assume that when the partial pressure of hydrothermal H_2 was locally high in the mound, it became adsorbed onto, or absorbed into, the Fe_4S_4 cubane of greigite where it lost its integrity (cf. nitrogenase, Fig. 7f; Einsle et al. 2002). Here it disassembled to a proton which attached itself to one of the sulfur atoms and an electron which was transferred to the delocalized electron cloud around the iron atoms, to leave a highly reactive hydrogen atom ($H\bullet$), much as it does in metallic iron and the ferredoxin proteins (Kjekshus et al., 1972; Cammack, 1996; Morita, 2000; Fig. 7a):



Activated thus, the hydrogen could attack the carbon dioxide (or bicarbonate), reducing it to CO and H_2O (Fig. 7a). In turn, reaction of the CO with methane thiol (CH_3SH) (Heinen and Lauwers, 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):



and



The CH_3SH 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 $Ni-2S-[Fe_4S_4]^+$ or $Fe-2S-[NiFe_3S_4]^{2+}$ were sequestered by the CH_3S^- to produce $SNiSFe_4S_4(CH_3S)_4^{3-}$ or $SFeSNiFe_3S_4(CH_3S)_4^{2-}$ 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 nanocrystals on the other. The system was now primed for the organic takeover.

Polymerization

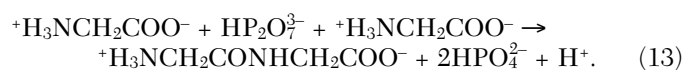
Whereas the simple amino acids and other modular organic compounds could have been produced by the reduction of CO_2 with hydrothermal NH_3 , H_2 , and CH_3S^- , their polymerization to a peptide required a surface, perhaps provided by mackinawite or clay (cf. Ferris et al., 1996). We speculate that peptides were first condensed from amino acids ($RCHNH_2COOH$; 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 ($-NH_3^+$) to form a peptide bond ($-NCHOC-$). The formation of a peptide bond may have been effected either by pyrophosphates or by the spontaneous loss of a thiol (RSH).

Here we consider the contribution of pyrophosphates to the polymerizing process. Beginning with acetyl phosphate ($CH_3COPO_4^{2-}$, generated by phosphorylation of the acetyl thioester produced in equation (10); de Duve, 1991) and inorganic monophosphate (HPO_4^{2-}), de Zwart et al. (2004) have produced pyrophosphate ($HP_2O_7^{3-}$) in aqueous conditions, using freshly precipitated FeS as catalyst and protective

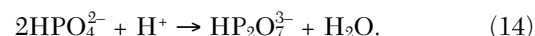
surface. An optimal 25 percent yield of pyrophosphate was achieved only between 38° and 51°C:



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:



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):



The protonmotive force is a fundamental chemical process in generating localized energy (Mitchell, 1967). 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 ($NH_3^+CH_2COO^-$) alternates with lysine ($NH_3^+CH_2(CH_2)_3NHCHCOO^-$) 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 $[Fe_4S_4]$ electron transfer sites (Tabushi et al., 1988), and structures such as $Ni-S_2-[Fe_4S_4]-S_2-Fe$ to catalyze the reaction between CO_2 and H_2 ,

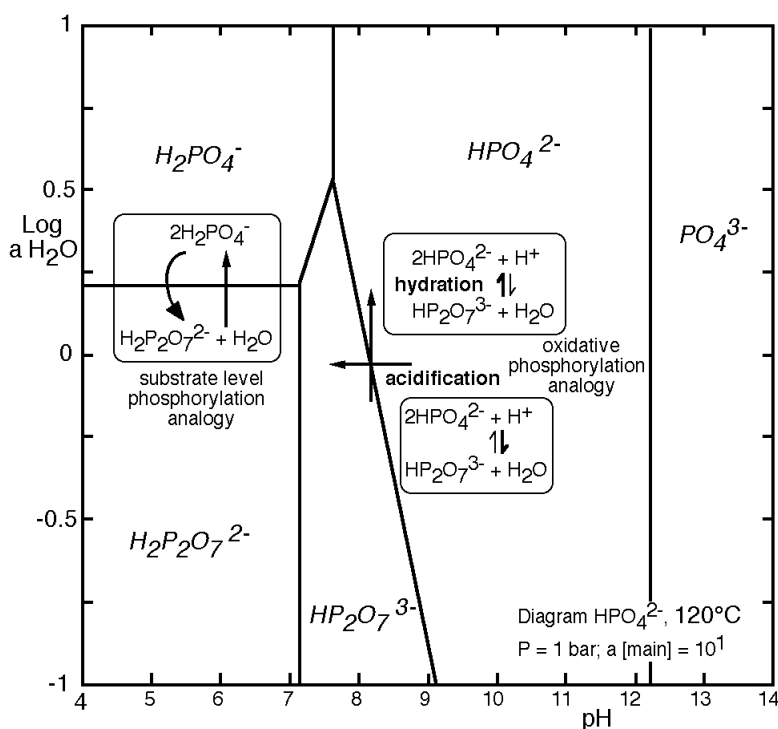


FIG. 8. pH vs. $\log a_{\text{H}_2\text{O}}$ diagram constructed using Geochemists Workbench (Bethke, 1996), illustrating the inorganic basis of life's main energy-transfer processes. High-energy phosphoanhydride ($\text{HP}_2\text{O}_7^{3-}$), stable at relatively low pH and water activity and relatively high temperature, can form from low-energy monophosphate (2HPO_4^{2-}). $\text{HP}_2\text{O}_7^{3-}$ can drive dehydration polymerizations on its hydration (cf. the $\text{ATP}^4/\text{ADP}^{3-}$ /or AMP^{2-} energy cycle of life in which an anhydride bond is formed to link phosphates). Energy released on the breaking of the pyrophosphate bond can be used to build organic polymers. In oxidative phosphorylation the dehydrating power of ATP can be renewed by the protonmotive force (acidification), whereas in substrate level phosphorylation ATP is renewed by removal of H^+ and OH^- by an NAD-associated enzyme (based on Russell and Hall, 1997; and see Table 1).

and CO and CH_3S^- . 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 $\text{NiS}_2\text{Fe}_4\text{S}_4(\text{CH}_3\text{S})\text{O}_4^{2-}$ and $\text{Fe}_4\text{S}_4(\text{RS})\text{O}_4^{2-/3-}$ 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 $\text{HP}_2\text{O}_7^{3-}$, or the organic adenosine triphosphate (ATP^{2-}) 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

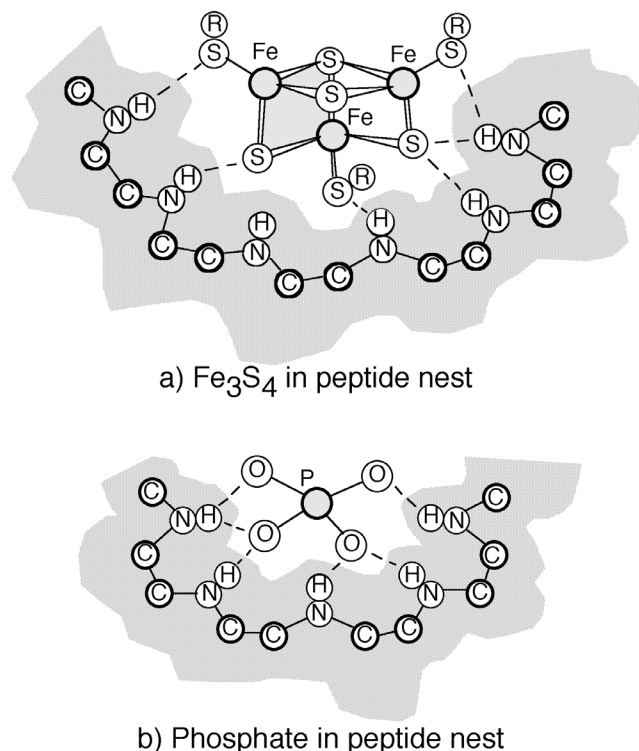


FIG. 9. Ball and stick sketches of peptide nests comprising alternating glycines with other abiotic amino acids binding (a) an Fe_3S_4 of a protoferredoxin, and (b) inorganic phosphate. Sequestering these inorganic complexes in this way is a step toward enzyme biochemistry. Based on Milner-White and Russell (2005).

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 adsorbed, 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 ($-\text{NH}_3^+$) of one amino acid to the carboxyl ($-\text{COO}^-$) or thiocarboxyl ($-\text{COS}^-$) 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 ($-(\text{CH}_2)_4\text{NH}_3^+$) to produce polylysine ($-(\text{NH}(\text{CH}_2)_4\text{CH}(\text{NH}_3^+)\text{CO}-)_n$, 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 ($-(\text{CH}_2)_2\text{SH.CH}_3$) 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 microcavities 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

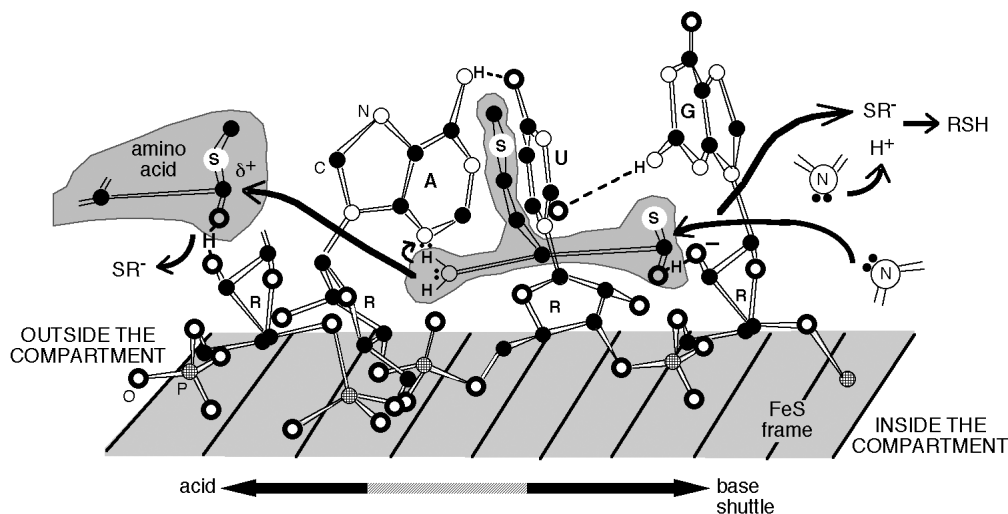


FIG. 10. Sketch to show how the present mechanism for amino-acid adsorption, polymerization, a crude coding, and subsequent release by acid-base catalysis (Muth et al., 2000) might have originated. In the case shown here, the side chains of three RNA monomers, comprising ribose sugar and the bases adenine (A), uracil (U), and guanine (G), which together constitute a triplet that codes for methionine, gripped the amino acid in such a way as to offer it to the adjacent amino acid for polymerization to a peptide. Dashed lines denote hydrogen bonds. Different sequences of RNA monomers in triplets happened to have affinities for different amino-acid side chains—amino acids with hydrophobic side chains will tend to dock in clefts where U is the central base, whereas those with hydrophilic side chains are attracted to triplets where A, or to a lesser degree, G is the central base. The process is assumed to have taken place in the relatively "dry" mackinawitic membrane that separated the acidulous Hadean ocean from warm alkaline seepage water. Based on Mellersh (1993) and Russell et al. (2003).

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 Fröh-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 Mn^{IV} and S^0 joined Fe^{III} as electron sinks accessible to unicellular microbes while still within the mound (Stetter and Gaag, 1983; Myers and Nealson, 1988; McFadden and Shively, 1991; Pace, 1997; Russell and Hall, 1997; Reysenbach and Lovley, 2002; Fig. 12).

The process of reduction of Mn^{IV} is similar to that of Fe^{III} 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. S^0 is insoluble but polysulfide (S_8), one of the products of SO_2 photolysis, is the substrate of sulfur respiration (Schauder and Kröger, 1993). Significant quantities of S_8 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

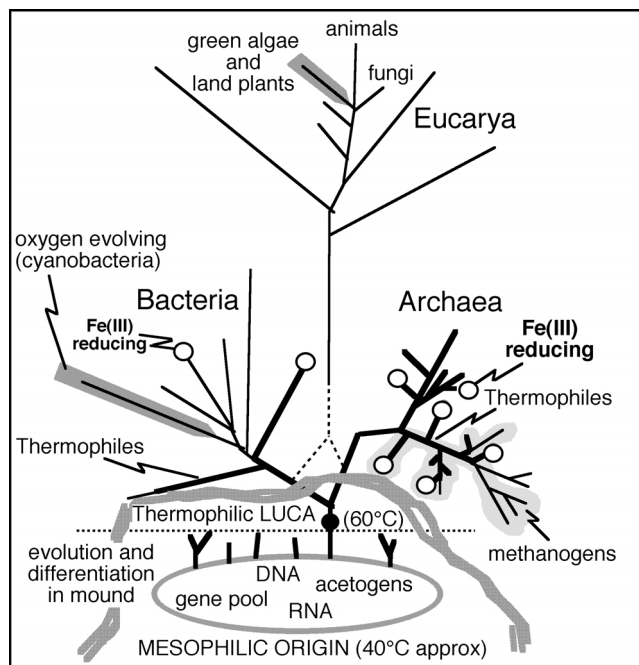


FIG. 11. The evolutionary tree based on Woese et al. (1990) and Stetter (1996). Many prokaryotes in the lowest branches of the tree can use Fe^{III} as an electron acceptor (Liu et al., 1997; Vargas et al., 1998; Reysenbach and Lovley, 2002). Note that methanogens are only found in the archaeobacterial domain and that oxygenic photosynthesis is a property of the cyanobacteria (in the bacterial domain), or of their derivative chloroplasts in the green algae and land plants in the eukaryotic domain (Martin et al., 2003). LUCA is the last common universal ancestor or ancestral community (Poole, 2002).

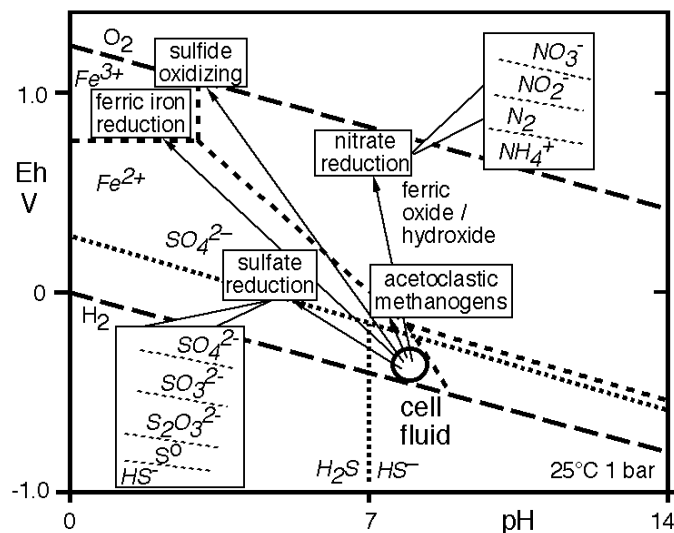


FIG. 12. Redox potential vs. pH showing electron transfer vectors between the cellular fluid (cytoplasm) of prokaryotes and their various electron acceptors. The background Pourbaix diagram, calculated using Geochemists Workbench (Bethke, 1996), shows the main stability fields of iron and sulfur species as a guide to the geochemistry of natural aqueous environments (based on Russell and Hall, 1997).

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 homoacetogens, initially suited to low to moderate temperatures, and the archaea, the methanogens, initially suited to higher temperatures. The homoacetogens gained, and continue to gain, their energy by the overall reaction:



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; Thae, 1998):



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



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 (Whitman 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, 1999; Rosing and Frei, 2003; Russell and Arndt, 2005). If this were the case, it follows that the majority of the currently known metabolic cycles 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 (Lécuyer 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 $([\text{Fe}_4\text{S}_4]4[\text{RS}])^{2-}$ and $\text{HP}_2\text{O}_7^{3-}$, and (5) surface-bonded 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 sinters (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_3S^- , NH_3 , Mg^{2+} , and trace amounts of CN^- . The remaining contribution was the CO_2 and $\text{HP}_2\text{O}_7^{3-}$, 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 $\text{Fe}(\text{Ni})\text{S}$, 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; Fallick et al., 2001).

July 25, 2004; March 24, 2005

REFERENCES

- Abbott, D.H., and Hoffman, S.E., 1984, Archaean plate tectonics revisited 1. The age of subducting oceanic lithosphere and their effects on the origin and evolution of continents: *Tectonics*, v. 3, p. 429–448.
- Adams, M.W.W., 1998, The evolutionary significance of the metabolism of tungsten by microorganisms growing at 100°C, in Wiegel, J., and Adams, M.W.W., eds., *Thermophiles: The keys to molecular evolution and the origin of life*: Washington, Taylor and Francis, p. 325–338.
- Allen, D.A., and Seyfried, W.E., 2003, Compositional controls on vent fluids from ultramafic-hosted hydrothermal systems at mid-ocean ridges: An experimental study at 400°C, 500 bars: *Geochimica et Cosmochimica Acta*, v. 67, p. 1531–1542.
- Amend, J.P., and Shock, E.L., 2001, Energetics of overall metabolic reactions of thermophilic and hyperthermophilic Archaea and bacteria: *FEMS Microbiology Reviews*, v. 25, p. 175–243.
- Ames, D.E., Watkinson, D.H., and Parrish, R.R., 1998, Dating of a regional hydrothermal system induced by the 1850 Ma Sudbury impact event: *Geology*, v. 26, p. 447–450.
- Anderson, R.B., Langseth, M.G., and Sclater, J.G., 1977, The mechanisms of heat transfer through the floor of the Indian Ocean: *Journal of Geophysical Research*, v. 82, p. 3391–3409.
- Armstrong, R.L., 1981, Radiogenic isotopes: The case for crustal recycling on a near-steady-state no-continental-growth Earth: *Philosophical Transactions of the Royal Society of London (ser. A)*, v. 301, p. 443–472.
- Arndt, N.T., 1998, Why was flood volcanism on submerged continental platforms so common in the Precambrian?: *Precambrian Research*, v. 97, p. 155–164.
- Arndt, N.T., and Chauvel, C., 1990, Crust of the Hadean Earth: *Bulletin Geological Society Denmark*, v. 39, p. 145–151.
- Bada, J.L., 2004, How life began on Earth: A status report: *Earth and Planetary Science Letters*, v. 226, p. 1–15.
- Bada, J.L., and Lazcano, A., 2002, Origin of life—some like it hot, but not the first biomolecules: *Science*, v. 296, p. 1982–1983.
- Bahcall, J.N., Pinsonneault, M.H., and Basu, S., 2001, Solar models: Current epoch and time dependences, neutrinos, and helioseismological properties: *Astrophysical Journal*, v. 555, p. 990–1012.
- Baltscheffsky, H., 1996, Energy conversion leading to the origin and early evolution of life: Did inorganic pyrophosphate precede adenosine triphosphate?, in Baltscheffsky, H., ed., *Origin and evolution of biological energy conversion*: Cambridge, VCH Publishers, p. 1–9.
- Banks, D., 1985, A fossil hydrothermal worm assemblage from the Tynagh lead-zinc deposit in Ireland: *Nature*, v. 313, p. 128–131.
- Banks, D.A., and Russell M.J., 1992, Fluid mixing during ore deposition at the Tynagh base-metal deposit, Ireland: *European Journal of Mineralogy*, v. 4, p. 921–931.
- Barrie, T.T., Erendi, A., and Cathles, L., 2001, Paleosea-floor volcanic-associated massive sulfide mineralization related to a cooling komatiite flow, Abitibi province, Canada: *ECONOMIC GEOLOGY*, v. 96, p. 1695–1700.
- Baymann, F., Lebrun, E., Brugna, M., Schoepp-Cothenet, B., Giudici-Ortoni, M.T., and Nitschke, W., 2003, The redox protein construction kit: Pre-last universal common ancestor evolution of energy-conserving enzymes: *Philosophical Transactions of the Royal Society of London*, v. 358B, p. 267–274.
- Bebbie, J., Schoonen, M.A.A., Fuhrmann, M., and Stongin, D.R., 1998, Surface charge development on transition metal sulfides: An electrokinetic study: *Geochimica et Cosmochimica Acta*, v. 62, p. 633–642.
- Bernal, J.D., 1960, The problem of stages in biopoiesis, in Florkin M. ed., *Aspects of the origin of life*: New York, Pergamon Press, p. 30–45.
- Bethke, C., 1996, *Geochemical reaction modeling*: New York, NY, Oxford University Press, 375 p.
- Bischoff, J.L., and Rosenbauer, R.J., 1985, An equation of state for hydrothermal seawater (3.2 percent NaCl): *American Journal of Science*, v. 285, p. 725–763.
- Bischoff, J.L., and Seyfried, W.E., 1978, Hydrothermal chemistry of seawater from 25° to 350°C: *American Journal of Science*, v. 278, p. 838–860.
- Bjerrum, C.J., and Canfield, D.E., 2002, Ocean productivity before about 1.9 Gyr ago limited by phosphorus adsorption onto iron oxides: *Nature*, v. 417, p. 159–162.
- Bonomi, F., Werth, M.T., and Kurtz, D.M., 1985, Assembly of $\text{Fe}_n\text{S}_m(\text{SR})^2$ ($n=2,4$) in aqueous media from iron salts, thiols and sulfur, sulfide, thiosulfide plus rhodanese: *Inorganic Chemistry*, v. 24, p. 4331–4335.
- Boyce, A.J., Coleman, M.L., and Russell, M.J., 1983, Formation of fossil hydrothermal chimneys and mounds from Silvermines, Ireland: *Nature*, v. 306, p. 545–550.
- Boyce, A.J., Little, C.T.S., and Russell, M.J., 2003, A new fossil vent biota in the Ballynoe barite deposit, Silvermines, Ireland: Evidence for intracratonic sea-floor hydrothermal activity about 352 Ma: *ECONOMIC GEOLOGY*, v. 98, p. 649–656.
- Braterman, P.S., Cairns-Smith, A.G., and Sloper, R.A., 1983, Photo-oxidation of hydrated Fe^{2+} : Significance for banded iron formations: *Nature*, v. 303, p. 163–164.
- Braun, D., and Libchaber, A., 2004, Thermal force approach to molecular evolution: *Physical Biology*, v. 1, p. 1–8 (DOI: 10.1088/1478-3967/1/1/P01), 8 p.
- Byerly, G.R., Lowe, D.R., Wooden, J.L., and Xie, X., 2002, An Archean impact layer from the Pilbara and Kaapvaal cratons: *Science*, v. 297, p. 1325–1327.
- Cairns-Smith, A.G., 1982, *Genetic takeover and the mineral origins of life*: Cambridge, New York, Cambridge University Press, 477 p.
- Cairns-Smith, A.G., Hall, A.J., and Russell, M.J., 1992, Mineral theories of the origin of life and an iron sulphide example: *Origins of Life and Evolution of the Biosphere*, v. 22, p. 161–180.
- Cammack, R., 1996, Iron and sulfur in the origin and evolution of biological energy conversion systems: in Baltscheffsky, H., ed., *Origin and evolution of biological energy conversion*: Cambridge, VCH Publishers, p. 43–69.
- Canfield, D.E., 1998, A new model for Proterozoic ocean chemistry: *Nature*, v. 396, p. 450–453.
- Canuto, V.M., Levine, J.S., Augustsson, T.R., and Imhoff, C.L., 1982, UV radiation from the young Sun and oxygen and ozone levels in the prebiological palaeoatmosphere: *Nature*, v. 296, p. 816–820.
- Cathles, L.M., 1983, An analysis of the hydrothermal system responsible for massive sulfide deposition in the Hokuroku basin of Japan: *ECONOMIC GEOLOGY MONOGRAPH* 5, p. 439–487.
- 1990, Scales and effects of fluid flow in the upper crust: *Science*, v. 248, p. 323–329.
- Catling, D.C., Zahnle, K.J., and McKay, C.P., 2001, Biogenic methane, hydrogen escape, and the irreversible oxidation of early Earth: *Science*, v. 293, p. 839–843.
- Cleaves, H.J., and Miller, S.L., 1998, Oceanic protection of prebiotic organic compounds from UV radiation: *Proceedings of the National Academy of Sciences of the United States of America*, v. 95, p. 7260–7263.
- Cody, G.D., 2004, Transition metal sulfides and the origin of metabolism: *Annual Review of Earth and Planetary Science*, v. 32, p. 569–599.
- Constantinou, G., and Govett, G.J.S., 1973, Geology, geochemistry, and genesis of Cyprus sulfide deposits: *ECONOMIC GEOLOGY*, v. 68, p. 843–858.
- Corliss, J.B., Baross, J.A., and Hoffman, S.E., 1981, An hypothesis concerning the relationship between submarine hot springs and the origin of life on Earth: *International Geological Congress, Geology of Oceans Symposium*, 26th, Paris, July 7–17, 1980, *Proceedings, Oceanologica Acta*, N° SP, p. 59–69.

- Darnault, C., Volbeda, A., Kim, E.J., Legrand, P., Vernède, X., Lindahl, P.A., and Fontecilla-Camps, J.C., 2003, Ni-Zn-[Fe₄-S₄] and Ni-Ni-[Fe₄-S₄] clusters in closed and open subunits of acetyl-CoA synthase/carbon monoxide dehydrogenase: *Nature Structural Biology*, v. 10, p. 271–279.
- Darwin, F., 1888, *The life and letters of Charles Darwin*: London, John Murray, v. 3, 418 p.
- Davies, G.F., 1992, On the emergence of plate tectonics: *Geology*, v. 20, p. 963–966.
- Davis, E.E., and Becker, K., 1999, Tidal pumping of fluids from the oceanic crust: New observations and opportunities for sampling the crustal hydrosphere: *Earth and Planetary Science Letters*, v. 172, p. 141–149.
- Deamer, D.W., 1985, Boundary structures are formed by organic components of the Murchison carbonaceous chondrite: *Nature*, v. 317, p. 792–794.
- De Duve, C., 1991, *Blueprint for a cell: The nature and origin of life*: Burlington, Neil Patterson, 275 p.
- De Ronde, C.E.J., 1995, Fluid chemistry and isotopic characteristics of seafloor hydrothermal systems and associated VMS deposits: Potential for magmatic contributions: *Mineralogical Association of Canada Short Course*, v. 23, p. 479–509.
- de Zwart, I.I., Meade, S.J., and Pratt, A.J., 2004, Biomimetic phosphoryl transfer catalysed by iron(II)-mineral precipitates: *Geochimica et Cosmochimica Acta*, v. 68, p. 4093–4098.
- Dobbeck, H., Svetlitchnyi, V., Gremer, L., Huber, R., and Meyer, O., 2001, Crystal structure of a carbon monoxide dehydrogenase reveals a [Ni-4Fe-5S] cluster: *Science*, v. 293, p. 1281–1285.
- Doukov, T.I., Iverson, T.M., Seravalli, J., Ragsdale, S.W., and Drennan, C.L., 2002, A Ni-Fe-Cu center in a bifunctional carbon monoxide dehydrogenase/acetyl-CoA synthase: *Science*, v. 298, p. 567–572.
- Douville, E., Charlou, J.L., Oelkers, E.H., Bienvu, P., Colon, C.F.J., Donval, J.P., Fouquet, Y., Priour, D., and Appriou, P., 2002, The Rainbow vent fluids (36°14'N, MAR): The influence of ultramafic rocks and phase separation on trace metal content in Mid-Atlantic Ridge hydrothermal fluids: *Chemical Geology*, v. 184, p. 37–48.
- Drennan, C.L., Heo, J., Sintchak, M.D., Schreiter, E., and Ludden, P.W., 2001, Life on carbon monoxide: X-ray structure of *Rhodospirillum rubrum* Ni-Fe-S carbon monoxide dehydrogenase: *Proceedings of the National Academy of Sciences of the United States of America*, v. 98, p. 11973–11978.
- Dymek, R.F., and Klein, C., 1988, Chemistry, petrology and origin of banded iron-formation lithologies from the 3800 Ma Isua supracrustal belt, West Greenland: *Precambrian Research*, v. 39, p. 247–302.
- Eck, R.V., and Dayhoff, M.O., 1966, Evolution of the structure of ferredoxin based on living relics of primitive amino acid sequences: *Science*, v. 152, p. 363–366.
- Einsle, O., Tezcan, F.A., Andrade, S.L.A., Schmid, B., Yoshida, M., Howard, J.B., and Rees, D.C., 2002, Nitrogenase MoFe-protein at 1.16 Å resolution: A central ligand in the FeMo-cofactor: *Science*, v. 297, p. 1696–1700.
- Faggerbakke, K.M., Haldal, M., and Norland, S., 1996, Content of carbon, nitrogen, oxygen, sulfur and phosphorus in native aquatic and cultured bacteria: *Aquatic Microbial Ecology*, v. 10, p. 15–27.
- Fallick, A.E., Ilich, M., and Russell, M.J., 1991, A stable isotope study of the magnetite deposits associated with the Alpine-type ultramafic rocks of Yugoslavia: *ECONOMIC GEOLOGY*, v. 86, p. 847–861.
- Fallick, A.E., Ashton, J.H., Boyce, A.J., Ellam, R.M., and Russell, M.J., 2001, Bacteria were responsible for the magnitude of the world-class hydrothermal base metal orebody at Navan, Ireland: *ECONOMIC GEOLOGY*, v. 96, p. 885–890.
- Farquhar, J., Savarino, J., Airieau, S., and Thiemens, M.H., 2001, Observation of wave-length sensitive mass-independent sulfur isotope effects during SO₂ photolysis: Implications for the early atmosphere: *Journal of Geophysical Research*, v. 106E, p. 32829–32839.
- Ferris, F.G., Jack, T.R., and Bramhill, B.J., 1992, Corrosion products associated with attached bacteria at an oil field water injection plant: *Canadian Journal of Microbiology*, v. 38, p. 1320–1324.
- Ferris, J.P., Hill, A.R., Liu, R., and Orgel, L.E., 1996, Synthesis of long prebiotic oligomers on mineral surfaces: *Nature*, v. 381, p. 59–61.
- Forterre, P., and Philippe, H., 1999, Where is the root of the universal tree of life?: *Bioessays*, v. 21, p. 871–879.
- Fox, S.W., Harada, K., and Rohlfing, D.L., 1962, The thermal copolymerization of amino acids, in Stahmann, M.A., ed., *Polyamino acids, polypeptides, and proteins*: Madison, Wisconsin, University of Wisconsin Press, p. 47–54.
- Früh-Green, G. L., Kelley D. S., Bernasconi, S. M., Karson, J. A., Ludwig, K. A., Butterfield, D. A., Boschi, C., and Proskurowski, G., 2003, 30,000 years of hydrothermal activity at the Lost City vent field: *Science*, v. 301, p. 495–498.
- Gaffey, M.J., 1997, *The early solar system: Origins of Life and Evolution of the Biosphere*, v. 27, p. 185–203.
- Garcia-Ruiz, J.M., Hyde, S.T., Camerup, A.M., Christy, A.G., Van Kranendonk, M.J., and Whelham, N.J., 2003, Self-assembled silica-carbonate structures and detection of ancient microfossils: *Science*, v. 302, p. 1194–1197.
- Geptner, A., Kristmannsdóttir, H., Kristjánsson, J.K., and Marteinson, V.T., 2002, Biogenic saponite from an active submarine hot spring, Iceland: *Clays and Clay Minerals*, v. 50, p. 174–185.
- Gilbert, W., 1986, *The RNA world*: *Nature*, v. 319, p. 618.
- Godderis, Y., and Veizer, J., 2000, Tectonic control of chemical and isotopic composition of ancient oceans: The impact of continental growth: *American Journal of Science*, v. 300, p. 434–461.
- Goldschmidt, V.M., 1937, The principles of distribution of chemical elements in minerals and rocks: *Journal of the Chemical Society*, v. 1937, p. 655–673.
- 1952, Geochemical aspects of the origin of complex organic molecules on Earth, as precursors to organic life: *New Biology*, v. 12, p. 97–105.
- Grosberg, A., 2002, Protein folding and the secret of life: *Physics World*, March, p. 26–27.
- Haeckel, E., 1892, *The history of creation*: Translated by E.R. Lankester Appleton, London, 422 p.
- Haldane, J.B.S., 1929, *The origin of life*: *Rationalist Annual*, v. 148, p. 3–10.
- Hannington, M.D., Galley, A.G., Herzig, P.M., and Petersen, S., 1998, A comparison of the TAG Mound and stockwork complex with Cyprus-type massive sulfide deposits: *Proceedings of the Ocean Drilling Program, Scientific Results*, v. 158, p. 389–415.
- Hannington, M.D., Herzig, P., Stoffers, P., Scholten, J., Garbe-Schonberg, D., Jonasson, I.R., Roest, W., and Shipboard Scientific Party, 2001, First high-temperature submarine hydrothermal vents and massive anhydrite deposits off the north coast of Iceland: *Marine Geology*, v. 177, p. 199–200.
- Heinen, W., and Lauwers, A.M., 1996, Organic sulfur compounds resulting from the interaction of iron sulfide, hydrogen sulfide and carbon dioxide in an anaerobic aqueous environment: *Origins of Life and Evolution of the Biosphere*, v. 26, p. 131–150.
- Hennet, R.J.-C., Holm, N.G., and Engel, M.H., 1992, Abiotic synthesis of amino acids under hydrothermal conditions and the origin of life: A perpetual phenomenon? *Naturwissenschaften*, v. 79, p. 361–365.
- Herzig, P.M., and Hannington, M.D., 2000, Input from the deep: Hot vents and cold seeps, in Schulz, H.D., and Zabel, M., eds., *Marine geochemistry*: Berlin, Springer-Verlag, p. 398–416.
- Holm, N.G., and Charlou, J.L., 2001, Initial indications of abiotic formation of hydrocarbons in the Rainbow ultramafic hydrothermal system, Mid-Atlantic Ridge: *Earth and Planetary Science Letters*, v. 191, p. 1–8.
- Huber, C., and Wächtershäuser, G., 1997, Activated acetic acid by carbon fixation on (Fe,Ni)S under primordial conditions: *Science*, v. 276, p. 245–247.
- 1998, Peptides by activation of amino acids on (Fe,Ni)S surfaces: Implications for the origin of life: *Science*, v. 281, p. 670–672.
- 2003, Primordial reductive amination revisited: *Tetrahedron Letters*, v. 44, p. 1695–1697.
- Humphris, S.E., and 24 others, 1995, The internal structure of an active seafloor massive sulphide deposit: *Nature*, v. 377, p. 713–716.
- Hunten, D.M., Turco, R.P., and Toon, O.B., 1980, Smoke and dust particles of meteoric origin in the mesosphere and stratosphere: *Journal of Atmospheric Science*, v. 37, p. 1342–1357.
- Isley, A.E., and Abbott, D.H., 1999, Plume-related mafic volcanism and the deposition of banded iron formation: *Journal of Geophysical Research*, v. 104, p. 15461–15477.
- Janecky, D.R., and Seyfried, W.E., 1983, The solubility of magnesium-hydroxide-sulfate-hydrate in seawater at elevated temperatures and pressures: *American Journal of Science*, v. 283, p. 831–860.
- Jernigan, R., Raghunathan, G., and Bahar, I., 1994, Characterization of interactions and metal ion binding sites in proteins: *Current Opinions in Structural Biology*, v. 4, p. 256–263.
- Josse, J., 1966, Constitutive inorganic pyrophosphatase of *Escherichia coli*. (II) Nature and binding of active substrate and the role of magnesium: *Journal of Biological Chemistry*, v. 241, p. 1948–1957.
- Joyce, G.F., 1989, RNA evolution and the origins of life: *Nature*, v. 338, p. 217–224.

- Kakegawa, T., Noda, M., and Nannri, H., 2002, Geochemical cycles of bio-essential elements on the early Earth and their relationships to the origin of life: *Resource Geology*, v. 52, p. 83–89.
- Kamber, B.Z., Moorbath, S., and Whitehouse, M.J., 2001, The oldest rocks on Earth: Time constraints and geological controversies: Geological Society of London Special Publications, v. 190, p. 177–203.
- Kasting, J.F., 1990, Bolide impacts and the oxidation state of carbon in the Earth's early atmosphere: *Origins of Life and Evolution of the Biosphere*, v. 20, 199–231.
- 1993, Earth's early atmosphere: *Science*, v. 259, p. 920–926.
- 2001, The rise of atmospheric oxygen: *Science*, v. 293, p. 819–820.
- Kelley, D.S., and Fröh-Green, G.L., 1999, Abiogenic methane in deep-seated mid-ocean ridge environments: Insights from stable isotope analyses: *Journal of Geophysical Research*, v. 104B, p. 10439–10460.
- Kelley, D.S., Karson, J.A., Blackman, D.K., et al., 2001, An off-axis hydrothermal vent field near the Mid-Atlantic Ridge at 30°N: *Nature*, v. 412, p. 145–149.
- Kjekshus, A., Nicholson, D.G., and Mukherjee, A.D., 1972, On the bonding in tetragonal FeS: *Acta Chemica Scandinavica*, v. 26, p. 1105–1110.
- Kling, G.W., Tuttle, M.L., and Evans, W.C., 1989, The evolution of thermal structure and water chemistry in Lake Nyos: *Journal of Volcanology and Geothermal Research*, v. 39, p. 151–165.
- Koga, Y., Kyuragi, T., Nishihara, M., and Sone, N., 1998, Did archaeal and bacterial cells arise independently from noncellular precursors? A hypothesis stating that the advent of membrane phospholipid with enantiomeric glycerophosphate backbones caused the separation of the two lines of descent: *Journal of Molecular Evolution*, v. 46, p. 54–63.
- Konecny, J., Schöninger, M., and Hofacker, G.L., 1995, Complementary coding conforms to the primeval comma-less code: *Journal of Theoretical Biology*, v. 173, p. 263–270.
- Krishnarao, J.S.R., 1964, Native nickel-iron alloy, its mode of occurrence, distribution and origin: *ECONOMIC GEOLOGY*, v. 59, p. 443–448.
- Lalou, C., Reys, J.-L., Brichet, E., Arnold, M., Thompson, C., Fouquet, Y., and Rona, P.A., 1993, New age data for Mid-Atlantic Ridge hydrothermal sites: TAG and Snakepit chronology revisited: *Journal of Geophysical Research*, v. 98, p. 9705–9713.
- Lécuyer, C., and Ricard, Y., 1999, Long-term fluxes and budget of ferric iron for the redox states of the Earth's mantle and atmosphere: *Earth and Planetary Science Letters*, v. 165, p. 197–211.
- Leduc, S., 1911, *The mechanism of life*: London, Rebman, 172 p.
- Leja, J., 1982, *Surface chemistry of froth flotation*: New York, Plenum Press.
- Lennie, A.R., and Vaughan, D.J., 1996, Spectroscopic studies of iron sulfide formation and phase relations at low temperatures: *Geochemical Society Special Publication 5*, p. 117–131.
- Liu, S.V., Zhou, J., Zhang, C., Cole, D.R., Gajdarziska-Josifovska, M., and Phelps, T.J., 1997, Thermophilic Fe(III)-reducing bacteria from the deep subsurface: the evolutionary implications: *Science*, v. 277, p. 1106–1109.
- Lowell, R.P., and Rona, P.A., 2002, Seafloor hydrothermal systems driven by serpentinization of peridotite: *Geophysical Research Letters*, v. 29, no. 11, 2002, DOI10.1029/2001GL014411, p. 1–4.
- Macalady, J., and Banfield, J.F., 2003, Molecular geomicrobiology: genes and geochemical cycling: *Earth and Planetary Science Letters*, v. 209, p. 1–17.
- Macleod, G., McKeown, C., Hall, A.J., and Russell, M.J., 1994, Hydrothermal and oceanic pH conditions of possible relevance to the origin of life: *Origins of Life and Evolution of the Biosphere*, v. 24, p. 19–41.
- Maher, K.A., and Stevenson, D.J., 1988, Impact frustration of the origin of life: *Nature* v. 331, p. 612–614.
- Maisonneuve, J., 1982, The composition of the Precambrian ocean waters: *Sedimentary Geology*, v. 31, p. 1–11.
- Marteinsson, V.T., Kristjánsson, J.K., Kristmannsdóttir, H., Dahlkvist, M., Sæmundsson, K., Hannington, M., Péttersdóttir, S.K., Gæptner, A., and Stoffers, P., 2001, Discovery of giant submarine smectite cones on the seafloor in Eyjafjörður, northern Iceland, and a novel thermal microbial habitat: *Applied and Environmental Microbiology*, v. 67, p. 827–833.
- Martin, W., and Russell, M.J., 2003, On the origin of cells: An hypothesis for the evolutionary transitions from abiotic geochemistry to chemoautotrophic prokaryotes, and from prokaryotes to nucleated cells: *Philosophical Transactions of the Royal Society of London*, v. 358B, p. 27–85.
- Martin, W., Rote, C., Hoffmeister, M., Theissen, U., Gelius-Dietrich, G., Ahr, S., and Henze, K., 2003, Early cell evolution, eukaryotes, anoxygenic sulfide, fungi first (?), and a tree of genomes revisited: *Life*, v. 55, p. 193–204.
- Maurette, M., Brack, A., Duprat, J., and Engrand, C., 2004, Delivery of micrometeoritic greenhouse gases and “smoke” particles during the post-lunar “late heavy bombardment” of the Earth [abs.]: Committee on Space Research (COSPAR) Scientific Assembly, 35th, Paris, 18–25 July, CD, Abstract 04-A-02754.
- McFadden, B.A., and Shively, J.M., 1991, Bacterial assimilation of carbon dioxide by the Calvin cycle, in Shively, J.M., and Barton, L.L., eds., *Variation in autotrophic life*: New York, Academic Press, p. 25–50.
- McGoldrick, P., 1999, Northern Australian “Sedex” Zn-Pb deposits: Microbial oases in Proterozoic seas, in Stanley, C.J. et al., eds. *Mineral deposits: Processes to processing*: Rotterdam, A.A. Balkema, p. 885–888.
- Mellersh, A.R., 1993, A model for the prebiotic synthesis of peptides which throws light on the origin of the genetic code and the observed chirality of life: *Origins of Life and Evolution of the Biosphere*, v. 23, p. 261–274.
- Mellersh, A.R., and Wilkinson, A.S., 2000, RNA bound to a solid phase can select an amino acid and facilitate subsequent amide bond formation: *Origins of Life and Evolution of the Biosphere*, v. 30, p. 3–7.
- Menon, S., and Ragsdale, S.W., 2000, Unleashing hydrogenase activity in carbon monoxide dehydrogenase/acetyl-CoA synthase and pyruvate:ferredoxin oxidoreductase: *Science*, v. 287, p. 1245–1247.
- Miller, S.L., and Urey, H.C., 1959, Organic compound synthesis on the primitive Earth: *Science*, v. 130, p. 245–251.
- Milner-White, E.J., and Russell, M.J., 2005, Nests as sites for phosphates and iron-sulfur thiolates in the first membranes: 3 to 6 residue anion-binding motifs: *Origins of Life and Evolution of the Biosphere*, v. 35, p. 19–27.
- Mitchell, P., 1967, Proton-translocation phosphorylation in mitochondria, chloroplasts and bacteria: *Natural fuel cells and solar cells: FASEB Journal*, v. 26, p. 1370–1379.
- Mojzsis, S.J., Coath, C.D., Greenwood, J.P., McKeegan, K.D., and Harrison, T.M., 2003, Mass-independent isotope effects in Archean (2.5 to 3.8 Ga) sedimentary sulfides determined by ion microprobe analysis: *Geochimica et Cosmochimica Acta*, v. 67, p. 1635–1658.
- Morel, F.M.M., and Hudson, R.J.M., 1985, The geobiological cycle of trace elements in aquatic systems: Redfield revisited, in Stumm, W., ed., *Chemical processes in lakes*: New York, Wiley-Interscience, p. 251–281.
- Morita, R.Y., 2000, Is H₂ the universal energy source for long-term survival?: *Microbial Ecology*, v. 38, p. 307–320.
- Morse, J.W., and Arakaki, T., 1993, Adsorption and coprecipitation of divalent metals with mackinawite (FeS): *Geochimica et Cosmochimica Acta*, v. 57, p. 3635–3640.
- Moulton, V., Gardner, P.P., Pointon, R.F., Creamer, L.K., Jameson, G.B., and Penny, D., 2000, RNA folding argues against a hot origin of life: *Journal of Molecular Evolution*, v. 51, p. 416–421.
- Muth, G.W., Orteleva-Donnelly, L., and Strobel, S.A., 2000, A single adenosine with a neutral pK_a in the ribosomal peptidyl transferase center: *Science*, v. 289, p. 947–950.
- Myers, C.R., and Nealson, K.H., 1988, Bacterial manganese reduction and growth with manganese oxide as the sole electron acceptor: *Science*, v. 240, p. 1319–1321.
- Neal, C., and Stanger, G., 1984, Calcium and magnesium hydroxide precipitation from alkaline groundwater in Oman, and their significance to the process of serpentinization: *Mineralogical Magazine*, v. 48, p. 237–241.
- Nilson, F.P.R., 2002, Possible impact of a primordial oil slick on atmospheric and chemical evolution: *Origins of Life and Evolution of the Biosphere*, v. 32, p. 247–253.
- Oparin, A.I., 1924, *Proiskhozhdenie Zhizny*: Moscow, Rabochii, 71 p.
- 1938, *Origin of life*: New York, MacMillan, 270 p.
- Orgel, L.E., 1986, RNA catalysis and the origins of life: *Journal of Theoretical Biology*, v. 123, p. 127–149.
- Orr, W., 1978, Sulfur, in Wedepohl, K.H., ed., *Handbook of Geochemistry*, Vol. II/2: Berlin, Springer-Verlag, p. 16-L-5.
- Oudin, E., and Constantinou, G., 1984, Black smoker chimney fragments in Cyprus sulphide deposits: *Nature*, v. 308, p. 349–353.
- Pace, N.R., 1997, A molecular view of microbial diversity and the biosphere: *Science*, v. 276, p. 734–740.
- 2002, The large scale topology of the tree of life [abs.]: *Astrobiology*, v. 2, p. 484.
- Palandri, J.L., and Reed, M.H., 2004, Geochemical models of metasomatism in ultramafic systems: Serpentinization, rodingitization, and sea floor carbonate chimney precipitation: *Geochimica et Cosmochimica Acta*, v. 68, p. 1115–1133.
- Parkes, R.J., Cragg, B.A., Fry, J.C., Herbert, R.A., and Wimpenny, J.W.T., 1990, Bacterial biomass and activity in deep sediment layers from the Peru margin: *Philosophical Transactions of the Royal Society of London*, v. 331A, p. 139–153.

- Parkes, R.J., Cragg, B.A., Bale, S.J., Getliff, J.M., Goodman, K., Rochelle, P.A., Fry, J.C., Weightman, A.J., and Harvey, S.M., 1994, Deep bacterial biosphere in Pacific Ocean sediments: *Nature*, v. 371, p. 410–413.
- Pavlov, A.A., and Kasting, J.F., 2002, Mass-independent fractionation of sulfur isotopes in Archean sediments: Strong evidence for an anoxic Archean atmosphere: *Astrobiology*, v. 2, p. 27–41.
- Poole, A.M., Jeffares, D.C., and Penny, D., 1999, Early evolution: prokaryotes, the new kids on the block: *BioEssays*, v. 21, p. 880–889.
- Rahman, L., 2002, The geochemical modelling of emergent life from submarine hydrothermal environments: Unpublished Ph.D. thesis, University of Glasgow, 193 p.
- Rasmussen, B., 2000, Filamentous microfossils in a 3,235-million-year-old volcanogenic massive sulphide deposit: *Nature*, v. 405, p. 676–679.
- Redfield, A.C., Ketchum, B.H., and Richards, F.A., 1963, The influence of organisms on the composition of seawater, in Hill, M.N., ed., *The sea*, v. 2: New York, Wiley-Interscience, p. 26–77.
- Reysenbach, A.L., and Lovley, D.R., 2002, *Geoglobus ahangari*, gen. nov., sp. nov., a novel hyperthermophile capable of oxidizing organic acids and growing autotrophically on hydrogen with Fe (III) serving as the sole electron acceptor: *International Journal of Systematic Evolutionary Microbiology*, v. 52, p. 719–728.
- Reysenbach, A.L., Seitzinger, S., Kirshtein, J., and McLaughlin, E., 1999, Molecular constraints on a high-temperature evolution of early life: *Biological Bulletin*, v. 196, p. 367–372.
- Ricardo, A., Carrigan, M.A., Olcott, A.N., and Benner, S.A., 2004, Borate minerals stabilize ribose: *Science*, v. 303, p. 196.
- Rickard, D., Butler, I.B., and Olroyd, A., 2001, A novel iron sulphide switch and its implications for earth and planetary science: *Earth and Planetary Science Letters*, v. 189, p. 85–91.
- Rohlfing, D.L., 1975, Coacervate-like microspheres from lysine-rich proteinoid: *Origins of Life and Evolution of the Biosphere*, v. 6, p. 203–209.
- Rosing, M.T., 1999, ¹³C-depleted carbon microparticles in >3700-Ma seafloor sedimentary rocks from West Greenland: *Science*, v. 283, p. 674–676.
- Rosing, M.T., and Frei, R., 2003, U-rich Archean sea-floor sediments from Greenland—indications of >3700 Ma oxygenic photosynthesis: *Earth and Planetary Science Letters*, v. 217, p. 237–244.
- Russell, M.J., 1988, Chimneys, chemical gardens and feldspar horizons ± pyrrhotine in some SEDEX deposits: Aspects of alkaline environments of deposition, in Zachrisson, E. ed., *Proceedings of the Seventh IAGOD (International Association on the Genesis of Ore Deposits) Symposium*: Stuttgart, Schweizerbart'sche, p. 59–66, 183–190.
- Russell, M.J., and Arndt, N.T., 2005, Geodynamic and metabolic cycles in the Hadean: *Biogeosciences*, v. 2, p. 97–111 <www.biogeosciences.net/bg/2/97/SRef-ID:1726-4189/bg/2005-2-97>.
- Russell, M.J., and Hall, A.J., 1997, The emergence of life from iron monosulphide bubbles at a submarine hydrothermal redox and pH front: *Journal of the Geological Society of London*, v. 154, p. 377–402.
- 2002, From geochemistry to biochemistry: Chemiosmotic coupling and transition element clusters in the onset of life and photosynthesis: *Geochemical News* 113, p. 6–12.
- Russell, M.J., and Martin, W., 2004, The rocky roots of the acetyl coenzyme-A pathway: *Trends in Biochemical Sciences*, v. 29, p. 358–363.
- Russell, M.J., Hall, A.J., Cairns-Smith, A.G., and Braterman, P.S., 1988, Submarine hot springs and the origin of life (correspondence): *Nature*, v. 336, p. 117.
- Russell, M.J., Hall, A.J., and Turner, D., 1989, In vitro growth of iron sulphide chimneys: Possible culture chambers for origin-of-life experiments: *Terra Nova*, v. 1, p. 238–241.
- Russell, M.J., Daniel, R.M., Hall, A.J., and Sherringham, J., 1994, A hydrothermally precipitated catalytic iron sulphide membrane as a first step toward life: *Journal of Molecular Evolution*, v. 39, p. 231–243.
- Russell, M.J., Daia, D.E., and Hall, A.J., 1998, The emergence of life from FeS bubbles at alkaline hot springs in an acid ocean, in Wiegel, J., and Adams, M.W.W., eds., *Thermophiles: The keys to molecular evolution and the origin of life*: Washington, Taylor and Francis, p. 77–126.
- Russell, M.J., Hall, A.J., and Mellersh, A.R., 2003, On the dissipation of thermal and chemical energies on the early Earth: The onsets of hydrothermal convection, chemiosmosis, genetically regulated metabolism and oxygenic photosynthesis, in Ikan, R., ed., *Natural and laboratory-simulated thermal geochemical processes*: Dordrecht, Kluwer, p. 325–388.
- Schauder, R., and Kröger, A., 1993, Bacterial sulphur respiration: *Archives of Microbiology*, v. 159, p. 491–497.
- Schink, B., 1997, Energetics of syntrophic cooperation in methanogenic degradation: *Microbiology and Molecular Biology Reviews*, v. 61, p. 262–280.
- Schulte, M.D. and Rogers, K.L., 2004, Thiols in hydrothermal solution: Standard partial molar properties and their role in the organic geochemistry of hydrothermal environments: *Geochimica et Cosmochimica Acta*, v. 68, p. 1087–1097.
- Schultz, A., and Elderfield, H., 1997, Controls on the physics and chemistry of seafloor hydrothermal circulation: *Philosophical Transactions of the Royal Society*, v. 355, p. 387–425.
- Scott, H.P., Hemley, R.J., Mao, H., Herschbach, D.R., Fried, L.E., Howard, W.M., and Bastea, S., 2004, Generation of methane in the Earth's mantle: In situ partial pressure-temperature measurements of carbonate reduction: *Proceedings of the National Academy of Sciences of the United States of America*, v. 101, p. 14023–14026.
- Seward, T.M., and Barnes, H.L., 1997, Metal transport by hydrothermal ore fluids, in Barnes, H.L., ed., *Geochemistry of hydrothermal ore deposits*: New York, John Wiley and Sons, p. 435–486.
- Seyfried, W.M., and Bischoff, J.L., 1981, Experimental seawater-basalt interaction at 300°C, 500 bars: Chemical exchange, secondary mineral formation, and implications for transport of heavy metals: *Geochimica et Cosmochimica Acta*, v. 45, p. 135–147.
- Shock, E.L., 1990, Geochemical constraints on the origin of organic compounds in hydrothermal systems: *Origins of Life and Evolution of the Biosphere*, v. 20, p. 331–367.
- 1992, Chemical environments of submarine hydrothermal systems: *Origins of Life and Evolution of the Biosphere*, v. 22, p. 67–107.
- Shock, E.L., and Schulte, M.D., 1998, Organic synthesis during fluid mixing in hydrothermal systems: *Journal of Geophysical Research*, v. 103E, p. 28513–28527.
- Shock, E.L., McCollom, T., and Schulte, M.D., 1998, The emergence of metabolism from within hydrothermal systems, in Wiegel, J., and Adams, M.W.W., eds., *Thermophiles: The keys to molecular evolution and the origin of life*: Washington, Taylor and Francis, p. 59–76.
- Sigurdsson, H., Devine, J.D., Tchoua, F.M., Presser, T.S., Pringle, M.K.W., and Evans, W.C., 1987, Origin of the lethal gas burst from Lake Monoun, Cameroon: *Journal of Volcanology and Geothermal Research*, v. 31, p. 1–16.
- Sleep, N.H., and Windley, B.F., 1982, Archean plate tectonics: Constraints and influences: *Journal of Geology*, v. 90, p. 363–379.
- Stetter, K.O., 1996, Hyperthermophilic procaryotes: *FEMS Microbiological Reviews*, v. 18, p. 149–158.
- Stetter, K.O., and Gaag, G., 1983, Reduction of molecular sulphur by methanogenic bacteria: *Nature*, v. 305, p. 309–311.
- Stevens, W.C., and Kurtz, D.M., 1985, Assembly of [Fe_nS_n(SPh)₄]²⁻ (n = 2,4) and their iron-thiolate precursors in aqueous media: *American Chemical Society Journal*, v. 24, p. 3444–3449.
- Svetlitchnyi, V., Dobbek, H., Meyer-Klaucke, W., Meins, T., Thiele, B., Römer, P., Huber, R., and Meyer, O., 2004, A functional Ni-Ni-[4Fe4S] cluster in the monomeric acetyl-CoA synthase from *Carboxydotherrmus hydrogenoformans*: *Proceedings of the National Academy of Sciences of the United States of America*, v. 101, p. 446–451.
- Tabushi, I., Kuroda, Y., and Sasaki, Y., 1988, Efficient electron transfer reaction catalyzed by synthetic Fe-S cluster in micelles: Its kinetic behavior and comparison with natural ferredoxin: *Tetrahedron*, v. 44, p. 2843–2854.
- Thauer, R.K., 1998, Biochemistry of methanogenesis: A tribute to Marjory Stephenson: *Microbiology*, v. 144, p. 2377–2406.
- Thauer, R.K., Jungermann, K., and Decker, K., 1977, Energy conservation in chemotrophic anaerobic bacteria: *Bacteriological Review*, v. 41, p. 100–180.
- Thorseth, I.H., Torsvik, T., Furnes, H., and Muehlenbachs, K., 1995, Microbes play an important role in the alteration of oceanic crust: *Chemical Geology*, v. 126, p. 137–146.
- Towe, K.M., 1990, Aerobic respiration in the Archean?: *Nature*, v. 348, p. 54–56.
- Turcotte D.L., 1980, On the thermal evolution of the Earth: *Earth and Planetary Science Letters*, v. 48, p. 53–58.
- Vargas, M., Kashefi, K., Blunt-Harris, E.L., and Lovely, D.R., 1998, Microbial evidence for Fe(III) reduction on early Earth: *Nature*, v. 395, p. 65–67.
- Vaughan, D.J., 1969, Nickelian mackinawite from Vlaktefontein, Transvaal: *American Mineralogist*, v. 54, p. 1190–1193.
- Vaughan, D.J., and Craig, J.R., 1978, Mineral chemistry of natural sulfides: Cambridge University Press, 493 p.

- Von Damm, K.L., 1990, Sea floor hydrothermal activity: Black smoker chemistry and chimneys: *Annual Review of Earth and Planetary Sciences*, v. 18, p. 173–204.
- 2000, Chemistry of hydrothermal vent fluids from 9°–10°N, East Pacific Rise: “Time zero,” the immediate post eruptive period: *Journal of Geophysical Research*, v. 105B, p. 11203–11222.
- Wächtershäuser, G., 1988a, Pyrite formation, the first energy source for life: A hypothesis: *Systematic Applied Microbiology*, v. 10, p. 207–210.
- 1988b, Before enzymes and templates: Theory of surface metabolism: *Microbiological Reviews*, v. 52, p. 452–484.
- Walker, J.C.G., 1985, Carbon dioxide on the early Earth: Origins of Life and Evolution of the Biosphere, v. 16, p. 117–127.
- Wellsbury, P., Goodman, K., Barth, T., Cragg, B.A., Barnes, S.P., and Parkes, R.J., 1997, Deep marine biosphere fuelled by increasing organic matter availability during burial and heating: *Nature*, v. 388, p. 573–576.
- Wenner, D.B., and Taylor, H.P., 1971, Temperatures of serpentinization of ultramafic rocks based on $^{18}\text{O}/^{16}\text{O}$ fractionation between coexisting serpentine and magnetite: *Contributions to Mineralogy and Petrology*, v. 32, p. 165–185.
- White, D.E., 1968, Environments of deposition of some base-metal deposits: *ECONOMIC GEOLOGY*, v. 63, p. 301–335.
- Whitehead, R.E.S., Davies, J.F., and Goodfellow, W.D., 1990, Isotopic evidence for hydrothermal discharge into anoxic seawater, Sudbury basin, Ontario, Canada: *Chemical Geology (Isotope Geoscience Section)*, v. 86, p. 49–63.
- Whitman, W.B., Coleman, D.C., and Wiebe, W.J., 1998, Prokaryotes: The unseen majority: *Proceedings of the National Academy of Sciences of the United States of America*, v. 95, p. 6578–6583.
- Woese, C.R., 1967, The genetic code: The molecular basis for genetic expression: New York, Harper and Row, 200 p.
- 1998, The universal ancestor: *Proceedings of the National Academy of Sciences of the United States of America*, v. 95, p. 6854–6859.
- Woese, C.R., Kandler, O., and Wheelis, M.L., 1990, Towards a natural system of organisms: Proposals for the domains Archaea, Bacteria, and Eucarya: *Proceedings of the National Academy of Sciences of the United States of America* v. 87, p. 4576–4579.
- Wolthers, M., Van der Gaast, S.J., and Rickard, D., 2003, The structure of disordered mackinawite: *American Mineralogist*, v. 88, p. 2007–2015.
- Xu, G., Wang, W., Groves, J.J., and Hecht, M.H., 2001, Self-assembled monolayers from a designed combinatorial library of *de novo*? *Proceedings of the National Academy of Sciences of the United States of America*, v. 98, p. 3652–3657.
- Yamagata, Y., Wanatabe, H., Saitoh, M., and Namba, T., 1991, Volcanic production of polyphosphates and its relevance to prebiotic evolution: *Nature*, v. 352, p. 516–519.
- Zedef, V., Russell, M.J., Hall, A.J., and Fallick, A.E., 2000, Genesis of sedimentary and vein-stockwork magnesite deposits in the ultramafic terrains of southwestern Turkey: A stable isotope study: *ECONOMIC GEOLOGY*, v. 95, p. 429–446.
- Zierenberg, R.A., Fouquet, Y., and Shipboard Scientific Party, 1998, The roots of a seafloor hydrothermal system: *Nature*, v. 392, p. 48.