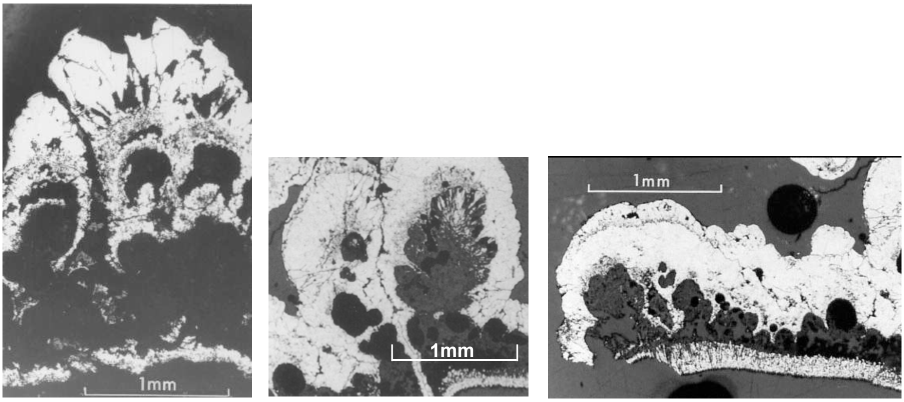

Fig. 6 Polished cross-sections of the Tynagh iron sulfide botryoids. These structures inspired the idea that the first compartments involved in the emergence of life were of comparable structure. It should be noted that the sulfide comprising what is now pyrite (FeS_2) in these 350 million-year-old submarine deposits was derived through bacterial sulfate reduction that took place in somewhat alkaline and saline seawater while the iron was contributed by exhaling acidic hydothermal solutions. On the early Earth the sulfide would have been carried in the alkaline solution as bisulfide, whereas the iron would have been contributed from the acidulous Hadean Ocean. On mixing, mackinawite (Fe(Ni)S) and greigite (Fe_5NiS_8) would have precipitated to form inorganic membranes at the interface (Russell et al. 1994; Russell and Hall 1997). Submarine mounds are invariably porous (Marteinsson et al. 2001; Kelley et al. 2005)

freeze-drying speeds up the curing of gels, that is, it demonstrates the effects of lithification without waiting on geological time. And they are remarkably similar to the Tynagh 'bubbles', even in detail (Russell et al. 1994, Fig. 6; Russell and Hall 1997, Fig. 5b, c) (Fig. 6).

(ii) *"We have no Hadean rocks that could show evidence for FeS-cells" and "As long as no valid empirical evidence is produced, a Hadean mound of FeS-cells must be considered unsubstantiated"*

(Wächtershäuser 2006, p 1808)

By definition, there are no Hadean sediments. As we have declared in numerous publications, indications that Hadean iron sulfide chimneys and botryoids may have formed then derives from the study of 350 million year old early Carboniferous Irish metal-sulfide ore deposits (Boyce et al. 1983, 2003). Moreover, two newly discovered active submarine alkaline hydrothermal mounds (of the kind predicted by the hypothesis, Russell et al. 1994) are entirely composed of porous precipitates comprising, in these cases, carbonate and clays—the kinds of deposit to be expected in present-day conditions (Kelley et al. 2001, 2005; Marteinsson et al. 2001).

(iii) *The FeS-cell experiments were done with a* $FeCl_2$ *solution of pH 1.9 (Russell et al.* 1989*). Acidity is crucial. Russell and Hall* (1997) *and Russell et al.* (1998, 2003) *calculated for the Hadean ocean pH 3.5, pH 4.5 (1998) or pH 5.5 (2003). This is anything but uncontroversial. Some geologists assume an alkaline Hadean ocean* (Maisonneuve 1982; Kempe and Degens 1985, 1989; Grotzinger 1994; Sukumaran 2000). *Others assume a nearly neutral Hadean ocean that developed from pH 5.6 at 100*°C *to pH 6.8 at* 70°C

(Morse and Mackenzie 1998). *Therefore, a Hadean ocean with a combination of a low temperature (less than 20*°C) *and an acidic pH, as required* (Russell et al. 2005) *may well be a geochemical impossibility*"

(Wächtershäuser 2006, p 1808).

The FeS-cell experiments were undertaken at a variety of pH conditions up to pH 5 in exploration for the kind of conditions that might reproduce such morphologies. The onus appears to be on Wächtershäuser to demonstrate that an acidulous ocean (pH 5–6) is a geochemical impossibility. Climatic and geochemical conditions are bound to have fluctuated quite violently on the early Earth. Nevertheless, the calculations concluding an acidulous Hadean ocean were advanced in Macleod et al. (1994). We note that the 10 bars of CO_2 in Lake Nyos in the Cameroon, our modern analogue, induces a pH approaching 5 (Russell and Hall 1997; Kusakabe et al. 2000). This level of acidity would have been further augmented by the sulfur dioxide produced by violent volcanism and meteoritic impacts and ultimately rained into the Hadean ocean as sulfuric acid, by volcanic HCl and by acid (pH 3) hot springs, ten times more numerous then than today (Lowell and Keller 2003). As to the idea of an early soda ocean, there is simply no known concentrating mechanism and no geological or geochemical support for this notion (Morse and Mackenzie 1998).

(iv) *"Russell and co-workers used in their chemical garden experiments concentrations of* $FeCl_2$ *of 3 wt% (1989) or 0.5 molar (1997), both by orders of magnitude too high". As long as no valid empirical evidence is produced, a Hadean mound of FeS-cells must be considered unsubstantiated"*

(Wächtershäuser 2006, p. 1808).

I concede that to reproduce the phenomenon of the botryoids and chimneys in the lab we have adopted a number of experimental approaches—normal practice in the early elucidation of origins. After all the Wächtershäuser experiments range in pH up to 12.8 (Huber and Wächtershäuser 2006), hardly matching conditions of the volcanic exhalations he appeals to for the site of life's emergence, though of course, more in keeping with our hypothesis (Russell 2003).

Wächtershäuser (2006, p 1808) also implies we should anyway defer to the seminal work of Hans Kuhn. From the kind of statement made in Kuhn and Kuhn (2003, p 263), [viz., "Thus even for the first steps suitable conditions must be found which lead to the aggregates of mutually compatible molecules and to the evolution of increasingly more complex and intricate structural diversity, temporal periodicity and spatial compartmentalization (e.g. day-night cycle and small pores in a rock) are fundamentally important conditions"], I find no particular resonance. The point about the submarine hydrothermal hatchery is that it grows fresh catalytic and chemically osmotic compartments at the same time as the proto-metabolic reductions, condensations and hydrolyses are assumed to take place, and in the dark. This submarine chemical and electrochemical reactor and affinity column is long-lived, chemostated, thermostated and self-restoring—it is not a bunch of passive unspecified rock pores.

While our hypothesis has developed and evolved we have not wavered in the basic tenets, i.e., of a warm alkaline hydrogen-bearing solution interfacing a carbonic ocean through a spontaneously precipitated catalytic barrier (Russell et al. 1988, 1989). And I would argue that most of the undoubted experimental successes of Wächtershäuser and his co-workers actually speak directly for the alkaline solution to the emergence of life and against an acidic origin at a volcanic exhalation. We recognize that one essential difference between the alkaline theory and Wächtershäuser's experimental findings lies in the source of carbon, whether volcanic CO (Wächtershäuser 2006; Huber and Wächtershäuser 2006; Ferry and House 2006) or CO_2 (Russell and Hall 1997; Russell and Martin 2004). Even here we have confessed uncertainty, wondering if CO_2 reduction wasn't initially a geochemical contribution, though of the alkaline hydrothermal system rather than from a distant volcano (Russell and Hall 1997, p 397; Martin and Russell 2007).

Another major difference is that Wächtershäuser's fixation reactions are putatively confined to the surface of a growing pyrite crystal (Wächtershäuser 1988b, 1990) whereas our assumed core reactions take place within the inorganic membrane and the products are then trapped within pores within the hydrothermal mound (Russell et al. 1988, 1994). Baaske et al. (2007) have now demonstrated how such products may be exponentially concentrated by thermophoresis within the cooler sections of the pores. Moreover, laminar convection within elongated pores could also have generated nucleic acid multimers (initially RNA) through the process of unfolding, melting (at ~100°C), annealing and elongation (at ~50°C) within clefts in a similar fashion to the albeit protein-catalyzed polymerase chain reaction (PCR) (Krishnan et al. 2002; Braun and Libchaber 2002, 2004).

Cody (2004) has compared both autogenic models in his review of the place of transition metal sulfides in the origin of metabolism.

20 Conclusions

Life is the chemical vortex that defies our vivocentric proclivities. Taking on the disequilibria that physics and chemistry could not resolve on our planet, life is a complex funnel for molecules such as CO_2 and H_2, unstable each to the other, produced by geochemical and/or photochemical processes and reliant on convection, to react, interact and ultimately be exhausted as one more transient drop in our lazy tiring, though partly complexifying Universe. The autogenic path into this chemical vortex, now a complex of coherent and genetically regulated metabolic cycles was, we contend, via early inorganic catalytic barriers or membranes, formed at an alkaline hydrothermal seepage and comprised in part of mixed valence iron sulfides doped with other transition elements such as nickel and molybdenum. These catalysts paved the way for the generation of acetate or methane, wastes from attractor systems that saw the synthesis of molecules entrained in further chemical reactions. Although evolution toward a takeover of membrane processes by proteins, and later by lipids, was probably rapid—minor concentrations of iron sulfides and traces of certain transition elements are vital to membrane processes to this day. That life had autogenic beginnings is not such an affront when we consider that the present food chain or web is grounded in the autotrophic fixation of atmospheric CO_2 with H_2 variously derived through chemosynthetic or photosynthetic reduction of CO_2 with H_2 from H_2O or H_2S respectively.

Although in dispute, it seems from the contrary requirements of kinetics and thermodynamics that the likely temperature of life's emergence was around 40°C (Moulton et al. 2000). Yet there is evidence to indicate that the last common surviving community thrived at 50 to 60°C or at even higher temperatures (Gaucher et al. 2003; Di Giulio 2003) perhaps a result of screening through a period of high ambient temperature caused either by bolide impacts or by the clearing of the skies and a reversion to a carbon dioxide greenhouse (Kasting and Akerman 1986; Kasting and Brown 1998; Nisbet and Sleep 2001; Schwartzman and Lineweaver 2005).

An early achievement of evolution was the decoupling of cells from the hydrothermal seepage site. Autonomous microbial communities could eventually prospect for fuels, carbon and metal sources elsewhere on and in the Earth. So from reliance on H_2, cells could fix CO_2 using organic detritus or other reduced entities such as H_2S (with S^0 as the waste). Much of this early evolution proceeded on and within the ocean floor. Then, born on the back of the advecting lithosphere, portions of the ocean floor and accompanying biosphere were obducted into the photic zone (Russell and Arndt 2005). Here, protected from hard UV by mineral grains, precursors to the green sulfur bacteria could have augmented the chemical energy supply of hydrothermal H_2S with solar photons (Phoenix et al. 2001; Baymann et al. 2001; Blankenship 2002). The extraordinary evolutionary jump to oxygenic synthesis was made possible by the redox sensitivity of a manganiferous component of the sediments. A mixed valence calcium manganite ($CaMn_4O_8$, cf., Barrier et al. 2005) could have been co-opted as a 'ready made' active center to facilitate the photolytic dissociation of two water molecules, gaining four electrons and four protons for biosynthesis in the process—ambient ferrous iron initially extracting the oxygen though eventually it was to escape as a waste gas (Allen 2005; Russell and Hall 2006; Yano et al. 2006; Allen and Martin 2007) (Table 1).

Metal-driven redox reactions are still responsible for a good proportion of the Earth's primary organic production. Much of this production is processed by phytoplankton even though the required metals are only available at less than 0.1 mM/l in today's aerobic oceans (Morel and Price 2003). Concentrations are greater in ocean bottom sediments where methanogens and acetogens still make up a large proportion of the Earth's biomass (Whitman et al. 1998) as they are in acid mine drainage (Baker and Banfield 2003). Although metals constitute the active centers of about one third of all known proteins, they were likely to have been involved in many more before "the great oxidation event", which happened when our planet was only half its present age. Even during the time of transition toward fully oxic conditions, the biophile trace metals were not limiting (Konhauser et al. 2002). But the first ocean, which condensed at ~4.4 Ga (Wilde et al. 2001) would have been strongly enriched in metal ions, supplied almost entirely through high temperature springs. In these early times we contend that metal complexes played many roles in the emergence of life and the production of the biosphere. They did so in conjunction with sulfides and phosphates. Indeed, to borrow a phrase from David Garner, "it is the inorganic elements that bring organic chemistry to life". Life then joined in the process aided by the conjugated bases, especially the nucleic acids (Martin and Russell 2007). Yet challenges and tests remain almost boundless in the experimental endeavor to demonstrate that, in principle, life could arise as a result of the abiogenic organization of inorganic matter and its organic products (Eschenmoser 1999).

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References

Abrajano TA, Sturchio NC, Kennedy BM, Lyon GL, Muehlenbachs K, Bohlke JK (1990) Geochemistry of reduced gas related to serpentinization of the Zambales ophiolite, Philippines. Appl Geochem 5: 625–630

Adams F (2002) Origins of existence: how life emerged in the universe. The Free Press, New York

Allen JF (2005) A redox switch hypothesis for the origin of two light reactions in photosynthesis. FEBS Lett 579: 963–968

Allen JF, Martin W (2007) Out of thin air. Nature 445:610–612

Allen JF, Puthiyaveetil S, Ström J, Allen CA (2005) Energy transduction anchors genes in organelles. BioEssays 27:426–435

Amend JP, Shock EL (2001) Energetics of overall metabolic reactions of thermophilic and hyperthermophilic Archaea and Bacteria. FEMS Microbiol Rev 25: 175–243

Ananyev GM, Zaltsman L, Vasko C and Dismukes GC (2001) The inorganic biochemistry of photosynthetic oxygen evolution/water oxidation. Biochim Biophys Acta 1503: 52–68

Apps JA and P.C. Van der Kamp (1993) Energy gases of abiogenic origin in the Earth's crust. The future of energy gases. US Geol Survey Prof Paper 1570: 81–132

Armstrong RL (1981) Radiogenic isotopes: the case for crustal recycling on a near-steady-state no-continental-growth Earth. Phil Trans Roy Soc Lond (Ser A) 301: 443–472

Armstrong RL (1991) The persistent myth of crustal growth. Aust J Earth Sci 38: 613–630

Azuma M, Hashimoto K, Hiramoto M, Watanabe M and Sakata T (1990) Electrochemical reduction of carbon dioxide on various metal electrodes in low-temperature aqueous $KHCO_3$ media. J Electrochem Soc 137: 1772–1778

Baaske P, Weinert F, Duhr S, Lemke K, Russell MJ, Braun D (2007) Extreme accumulation of nucleotides in simulated hydrothermal pore systems. Proc Natl Acad Sci USA 104:9346–9351

Bach W, Paulick H, Garrido CJ, Ildefonse B, Meurer WP, Humphris SE (2006) Unraveling the sequence of serpentinization reactions: petrography, mineral chemistry, and petrophysics of serpentinites from MAR 15°N (ODP Leg 209, Site 1274). Geophys Res Lett 33:L13306, doi:10.1029/2006GL025681

Baker BJ, Banfield JF (2003) Microbial communities in acid mine drainage. FEMS Microbiol Ecol 44:139–152

Ban N, Nissen P, Hansen J, Moore PB, Steitz TA (2000) The complete atomic structure of the large ribosomal subunit at 2.4 Å resolution. Science 289: 905–920

Barnes I., O'Neil JR, Trescazes JJ (1978) Present day serpentinization in New Caledonia, Oman, and Yugoslavia. Geochim Cosmochim Acta 42:144–145

Barney BM, Igarashi RY, Dos Santos PC, Dean DR, Seefeldt LC (2004) Substrate interaction at an iron–sulfur face of the FeMo-cofactor during nitrogenase catalysis. J Biol Chem 279: 53621–53624

Baross JA, Hoffman SE (1985) Submarine hydrothermal vents and associated gradient environments as sites for the origin and evolution of life. Orig Life Evol Biosph 15:327–345

Barrier N, Michel C, Maignan A, Hervieu M, Raveau B (2005) $CaMn_4O_8$, a mixed valence manganite with an original tunnel structure. J Mater Chem 15: 386–393

Baymann F, Brugna M, Mühlenhoff U, Nitschke W (2001) Daddy, where did (PS)I come from? Biochim Biophys Acta 1507:291–310

Baymann F, Lebrun E, Brugna M, Schoepp-Cothenet B, Giudici-Orticoni M-T, Nitschke W (2003) The redox protein construction kit: pre-last universal common ancestor evolution of energy-conserving enzymes. Phil Trans Roy Soc Lond (Ser B) 358:267–274

Beaumont V, Robert F (1998) Nitrogen isotope composition of organic matter from Precambrian cherts: new keys for nitrogen cycle evolution? Bull-Soc Geol France 169: 211–220

Bekker A, Holland HD, Wang PL, Rumble D, Stein HJ, Hannah JL, Coetzand LL, Beukes NJ (2004) Dating the rise of atmospheric oxygen. Nature 427: 117–120

Berg JM, Tymoczko JL, Stryer L (2007) Biochemistry. W.H. Freeman, New York

Bernal JD (1960) The problem of stages in biopoesis. In: Florkin M (ed) Aspects of the origin of life. Pergamon Press, New York, pp 30–45

Bischoff JL, Seyfried WE (1978) Hydrothermal chemistry of seawater from 25 to 350°C. Am J Sci 278:838–860

Bjerrum CJ, Canfield DE (2002) Ocean productivity before about 1.9 Gyr ago limited by phosphorus adsorption onto iron oxides. Nature 417:159–162

Black S (2000) A theory on the origin of life plus a brief history of biochemistry. Vantage Press, New York

Blake S (2003) Correlations between eruption magnitude, SO_2 yield, and surface cooling. In: Oppenheimer C, Pyle DM, Barclay J (eds) Volcanic degassing. Geological Society of London Special Publication 213, pp 371–380

Blankenship RE (2002) Molecular Mechanisms of Photosynthesis. Blackwell Science, Oxford

Bonomi F, Werth MT, Kurtz DM (1985) Assembly of $Fe_nS_n(SR)^{2-}$ (n = 2,4) in aqueous media from iron salts, thiols and sulfur, sulfide, thiosulfide plus rhodonase. Inorg Chem 24:4331–4335

Bowring SA, Williams IS (1999) Priscoan (4.00-4.03 Ga) orthogneisses from northwest Canada. Contrib Mineral Petrol 134:3–16

Boyce AJ, Coleman ML, Russell MJ (1983) Formation of fossil hydrothermal chimneys and mounds from Silvermines, Ireland. Nature 306: 545–550

Boyce AJ, Little CTS, Russell MJ (2003) A new fossil vent biota in the Ballynoe barite deposit, Silvermines, Ireland: Evidence for intracratonic sea-floor hydrothermal activity about 352 Ma. Econ Geol 98:649–656

Boyington JC, Gladyshev VN, Khangulov SV, Stadtman TC, Sun PD (1997) Crystal structure of formate dehydrogenase H: catalysis involving Mo, molybdopterin, selenocysteine, and an Fe_4S_4 cluster. Science 275: 1305–1308

Braterman PS, Cairns-Smith AG, Sloper RA (1983) Photo-oxidation of hydrated Fe^{2+}—significance for banded iron formations. Nature 303: 163–164

Braun D, Libchaber A (2002) Trapping of DNA by thermophoretic depletion and convection. Phys Rev Lett 89: 188103

Braun D, Libchaber A (2004) Thermal force approach to molecular evolution. Phys Biol 1: 1–8

Breslow R (1959) On the mechanism of the formose reaction. Tetrahedron Lett 21: 22–26

Brink H-J (2006) Do the global geodynamic cycles of the Phanerozoic represent afeedback system of the Earth and is the Moon involved as an acting external force? Z dt Ges Geowiss 157/1:17–40

Brochier C, Philippe H (2002) A non-hyperthermophilic ancestor for bacteria. Nature 417: 244

Cairns-Smith AG (1982) Genetic takeover and the mineral origins of life. Cambridge University Press, Cambridge, UK

Cairns-Smith AG, Hall AJ, Russell MJ (1992) Mineral theories of the origin of life and an iron sulphide example. Orig Life Evol Biosph 22: 161–180

Caldeira K, Kasting JF (1992) Susceptibility of the early Earth to irreversible glaciation caused by carbon dioxide clouds. Nature 359: 226–228

Cameron AGW (1963) The formation of the sun and planets. Icarus 1: 13–69

Cammack R, Frey M, Robson R (2001) Hydrogen as a fuel: learning from nature. Taylor & Francis, London

Canup RM, Agnor CB (2000) Accretion of the terrestrial planets and the earth-moon system. In: Canup RM, Righter K (eds) Origin of the earth and moon. Univ of Arizona Press, Tucson, pp 113–129

Canuto VM, Levine JS, Augustsson TR, Imhoff CL (1982) UV radiation from the young Sun and oxygen and ozone levels in the prebiological palaeoatmosphere. Nature 296: 816–820

Catling DC, Claire MW (2005) How Earth's atmosphere evolved to an oxic state: a status report. Earth Planet Sci Lett 23:1–20

Catling DC, Zahnle KJ, McKay CP (2001) Biogenic methane, hydrogen escape, and the irreversible oxidation of early Earth. Science 293: 839–843

Catling DC, Glein CR, Zahnle KJ, McKay CP (2005)Why O_2 is required by complex life on habitable planets and the concept of planetary “oxygenation time”. Astrobiology 5: 415–438
Chapelle FH, O’Neill K, Bradley PM, Methé BA, Ciufo SA, Knobel L-RL, Lovley DR (2002) A hydrogen-based subsurface microbial community dominated bymethanogens. Nature 415:312–315
Claypool GE, Kaplan LR (1974) The origin and distribution of methane in marine sediments. In: Kaplan LR (ed) Natural gases in marine sediments. Plenum Press, New York, pp 94–139
Cockell CS (2006) The origin and emergence of life under impact bombardment. Phil Trans Roy Soc (Ser B) 361:1845–1856
Cockell CS, Knowland J (1999) UV radiation screening compounds. Biol Rev 74: 311–345
Cody GD (2004) Transition metal sulfides and the origin of metabolism. Ann Rev Earth Planet Sci 32:569–599
Cody GD, Boctor NZ, Filley TR, Hazen RM, Scott JH, Sharma A, Yoder HS (2000) Primordial carbonylated iron–sulfur compounds and the synthesis of pyruvate. Science 289:1337–1340
Cody GD, Boctor NZ, Hazen RM, Brandes JA, Morowitz HJ, Yoder HS (2001) Geochemical roots of autotrophic carbon fixation: hydrothermal experiments in the system citric acid, $H_2O-(\pm FeS)-(\pm NiS)$. Geochim Cosmochim Acta 65: 3557–76
Coleridge ST (1795) The Æolian Harp. In Mays JCC (ed) The collected works of Samuel Taylor Coleridge, Vol 16, Poetical works. Part 1. Poems, 2001. Princeton University Press, Princeton, pp 231–233
Connell GJ, Illangasekare M, Yarus M (1993) Three small ribooligonucleotides with specific arginine sites. Biochem 32:5497–5502
Copley RR, Barton GJ (1994) A structural analysis of phosphate and sulphate binding sites in proteins: estimation of propensities for binding and conservation of phosphate binding sites. J Mol Biol 242: 321–329
Copley SD, Smith E, Morowitz HJ (2005) A mechanism for the association of amino acids with their codons and the origin of the genetic code. Proc Natl Acad Sci USA 102:4442–4447
Corliss JB (1986) On the creation of living cells in submarine hot spring flow reactors: attractors and bifurcations in the natural hierarchy of dissipative systems. Orig Life Evol Biosph 16: 381–382
Corliss JB, Baross JA, Hoffmann SE (1981) An hypothesis concerning the relationship between submarine hot springs and the origin of life on Earth. Oceanol Acta 4(Suppl):59–69
Corning PA, Kline SJ (1998) Thermodynamics, information and life revisited, Part I: ‘To be or entropy’. Syst Res 15:273–295
Conn MM, Prudent JR, Schultz PG (1996) Porphyrin metalation catalyzed by a small RNA molecule. J Am Chem Soc 118:7012–7013
Coveney RM, Goebel ED, Zeller EJ, Dreschhoff GAM, Angino EE (1987) Serpentinization and the origin of hydrogen gas in Kansas. Bull Am Assoc Petrol Geol 71:39–48
Crabtree RH (1997) Where smokers rule. Science 276: 222
Dagan T, Martin W (2007) Ancestral genome sizes specify the minimum rate of lateral gene transfer during prokaryote evolution. Proc Natl Acad Sci USA 104: 870–875
Dance I (2005) The hydrogen chemistry of the FeMo-co active site of nitrogenase. J Am Chem Soc 127: 10925–10942
Darnault C, Volbeda A, Kim EJ, Legrand P, Vernède X, Lindahl PA, Fontecilla-Camps JC (2003) Ni-Zn-[Fe4-S4] and Ni-Ni-[Fe4-S4] clusters in closed and open α-subunits of acetyl-CoA synthase/carbon monoxide dehydrogenase. Nat Struct Biol 10: 271–279
Davey ME, O’Toole GA (2000) Microbial biofilms: from ecology to molecular genetics. Microbiol Mol Biol Rev 64: 847–867
Davis EE, Becker K (1999) Tidal pumping of fluids from the oceanic crust: new observations and opportunities for sampling the crustal hydrosphere. Earth Planet Sci Lett 172:141–149
de Souza-Barros F, Braz-Levigard R, Ching-San Y, Monte MMB, Bonapace JAP, Montezano V, Vieyra A (2007) Phosphate sorption and desorption on pyrite in primitive aqueous scenarios: relevance of acidic → alkaline transitions. Orig Life Evol Biosph 37: 27–45
de Zwart II, Meade SJ, Pratt AJ (2004) Biomimetic phosphoryl transfer catalysed by iron(II)-mineral precipitates. Geochim Cosmochim Acta 68: 4093–4098
Delano JW (2001) Redox history of the Earth’s interior since 3900 Ma: implications for prebiotic molecules. Orig Life Evol Biosph 31: 311–341
DeLillo D (1998) Underworld. Picador, New York

Dewar R (2003) Information theory explanation of the fluctuation theorem, maximum entropy production and self-organized criticality in non-equilibrium stationary states. J Phys A Math Gen 36:631–641

DeWulf DW, Jin T, Bard AJ (1989) Electrochemical and surface studies of carbon dioxide reduction to methane and ethylene at copper electrodes in aqueous solutions. J Electrochem Soc 136:1686–1691

Di Giulio M (2003) The universal ancestor was a thermophile or a hyperthermophile: tests and further evidence. J Theor Biol 221:425–436

Dobbeck H, Svetlitchnyi V, Gremer L, Huber R, Meyer O (2001) Crystal structure of a carbon monoxide dehydrogenase reveals a [Ni-4Fe-5S] cluster. Science 293: 1281–1285

Doolittle WF (1999) Phylogenetic classification and the universal tree. Science 284:2124–2128

Doukov TI, Iverson TM, Seravalli J, Ragsdale SW, Drennan CL (2002) A Ni–Fe–Cu center in a bifunctional carbon monoxide dehydrogenase/acetyl-CoA synthase. Science 298:567–572

Douville E, Charlou JL, Oelkers EH, Bienvenu P, Colon CFJ, Donval JP, Fouquet Y, Prieur D, 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. Chem Geol 184:37–48

Drennan CL, Heo J, Sintchak MD, Schreiter E, Ludden PW (2001) Life on carbon monoxide: X-ray structure of *Rhodospirillium rubrum* Ni–Fe–S carbon monoxide dehydrogenase. Proc Natl Acad Sci USA 98: 11973–11978

Dunnill P (1966) Triplet nucleotide aminoacid pairing: a stereochemical basis for the division between protein and non protein aminoacids. Nature 210: 1267–1268

Eck RV, Dayhoff MO (1966) Evolution of the structure of ferredoxin based on living relics of primitive amino acid sequences. Science 152:363–366

Eigen M, Schuster P (1978) The hypercycle: a principle of natural self-organization. Part C. The realistic hypercycle. Naturwissenschaften 65:347–369

Eikerling M, Kornyshev AA, Kucernak AR (2006) Water in polymer electrolyte fuel cells: friend or foe? Phys Today, October, pp 38–44

Einsle O, Tezcan FA, Andrade SLA, Schmid B, Yoshida M, Howard JB, Rees DC (2002) Nitrogenase MoFe-protein at 1.16 Å resolution: a central ligand in the FeMo-cofactor. Science 297:1696–1700

Ellis RJ (2001) Macromolecular crowding: obvious but underappreciated. Trends Biochem Sci. 26: 597–604

Eschenmoser A (1988) Vitamin B12: experiments concerning the origin of its molecular structure. Angew Chem (Int Ed Engl) 27: 5–39

Eschenmoser A (1999) Chemical etiology of nucleic acid structure. Science 284:2118– 2124

Essene EJ, Fisher DC (1986) Lightning strike fusion: extreme reduction and metal-silicate liquid immiscibility. Science 234: 189–193

Farias ST, Moreira CH, Guimarães RC (2007) Structure of the genetic code suggested by the hydropathy correlation between anticodons and amino acid residues. Orig Life Evol Biosph 37:83–103

Farquhar J, Wing BA (2003) Multiple sulfur isotopes and the evolution of the atmosphere. Earth Planet Sci Lett 213:1–13

Farquhar J, Bao H, Thiemens MH (2000) Atmospheric influence of Earth’s earliest sulfur cycle. Science 289:756–758

Ferrer M, Golyshina OV, Beloqui1 A, Golyshin PN, Timmis KN (2007) The cellular machinery of Ferroplasma acidiphilum is iron-protein-dominated. Nature 445: 91–94

Ferris FG, Jack TR, Bramhill BJ (1992) Corrosion products associated with attached bacteria at an oil field water injection plant. Can J Microbiol 38: 1320–1324

Ferris JP, Hill AR, Liu R, Orgel LE (1996) Synthesis of long prebiotic oligomers on mineral surfaces. Nature 381: 59–61

Ferry JG, House CH (2006) The step-wise evolution of early life driven by energy conservation. Mol Biol Evol 23:1286–1292

Filtness MJ, Butler IB, Rickard D (2003) The origin of life: the properties of iron sulphide membranes. Trans Inst Mining Metall Appl Earth Sci 112B:171–172

Fisher AT (2005) Marine hydrogeology: recent accomplishments and future opportunities. Hydrogeol J 13: 69–97

Fontecilla-Camps JC, Ragsdale SW (1999) Nickel–iron–sulfur active sites: hydrogenase and CO dehydrogenase. Adv Inorg Chem 47:283–333

Fox SW (1959) Biological overtones of the thermal theory of biochemical origins. Bull Am Inst Biol Sci 9:20–23

Früh-Green GL, Kelley DD, Bernascono SM et al. (2003) 30,000 years of hydrothermal activity at the Lost City vent field. Science 301:495–498
Fuchs G (1989) Alternative pathways of autotrophic CO_2 fixation. In: Schlegel HG, Bowien B (eds) Autotrophic bacteria. Science Tech, Madison, WI, pp 365–382
Fuchs G (1994) Variations of the acetyl-CoA pathway in diversely related microorganisms that are not acetogens. In: Drake G (ed) Acetogenesis. Chapman & Hall, New York, pp 506–538
Fuchs G (1999a) Biosynthesis of building blocks. In: Lengeler JW, Drews G, Schlegel HG (eds) Biology of the prokaryotes. Stuttgart, Thieme, pp 110–160
Fuchs G (1999b) Assimilation of macroelements and microelements In: Lengeler JW, Drews G, Schlegel HG (eds) Biology of the prokaryotes. Stuttgart, Thieme, pp 163–186
Fusz S, Eisenführ A, Srivatsan SG, Heckel A, Famulok M (2005) A ribozyme for the aldol reaction. Chem Biol 12:941–950
Gaffey MJ (1997) The early solar system. Orig Life Evol Biosph 27: 185–203
Gaines SM (2001) Carbon Dreams. Creative Arts Book Company, Berkeley, CA
Gaucher EA, Thomson JM, Burgan M, Benner SA (2003) Inferring the palaeoenvironment of ancient bacteria on the basis of resurrected proteins. Nature 425: 285–288
Geptner A, Kristmannsdöttir H, Kristjánsson JK, Marteinsson VTh (2002) Biogenic saponite from an active submarine hot spring, Iceland. Clays Clay Miner 50: 174–185
Glasby GP (1998) Earliest life in the Archean: rapid dispersal of CO_2-utilizing bacteria from submarine hydrothermal vents. Episodes, pp 252–256
Goldschmidt VM (1952) Geochemical aspects of the origin of complex organic molecules on Earth, as precursors to organic life. New Biol 12:97–105
Griffin GW (1977) Ozone and oxides of nitrogen production during thunderstorms. J Geophys Res 82: 943–950
Grotzinger JP (1994) Trends in Precambrian carbonate sediments and their implication for understanding evolution. In: Bengtson S (ed) Early life on Earth: Nobel symposium 84. Columbia University Press, New York, pp 245–258
Gurevich AV, Zybin KP (2005) Runaway breakdown and the mysteries of lightning. Phys Today, May, pp 37–43
Haeckel E (1870) Natürliche schöpfungsgeschichte: Gemeinverständliche wissenschaftliche vorträge über die entwickelungslehre im allgemeinen und diejenige von Darwin, Goethe und Lamarck im besonderen, über die anwendung derselben auf den ursprung des menschen und andere damit zusammenhängende grundfragen der naturwissenschaft. Georg Reimer, Berlin, 688 p
Haeckel E (1876) The history of creation: or the development of the Earth and its inhabitants by the action of natural causes, a popular exposition of evolution in general, and that of Darwin, Goethe and Lamark in particular, Vol 1, translated by E.R. Lankester. Henry S. King & Co., London, 374 p
Hagan WJ, Parker A, Steuerwald A, Hathaway M (2007) Phosphate solubility and the cyanate-mediated synthesis of pyrophosphate. Orig Life Evol Biosph 37:113–122
Hall DO, Cammack R, Rao KK (1971) Role for ferredoxins in the origin of life and biological evolution. Nature 233: 136–138
Hartman H (1975) Speculations on the origin and evolution of metabolism. J Mol Evol 4:359–370
Harvey RB (1924) Enzymes of thermal algae. Science 50: 481–482
Hayes JM, Waldbauer JR (2006) The carbon cycle and associated redox processes through time. Phil Trans Roy Soc Lond (Ser. B) 361:931–950
Heath C, Lahaye Y, Stone WE, Lambert DD (2001) Origin of variations in nickel tenor along the strike of the Edwards lode nickel sulfide orebody, Kambalda, Western Australia. Can Mineral 39: 655–671
Heinen W, Lauwers AM (1996) Organic sulfur compounds resulting from the interaction of iron sulfide, hydrogen sulfide and carbon dioxide in an anaerobic aqueous environment. Orig Life Evol Biosph 26: 131–150
Heinen W, Lauwers AM (1997) The iron–sulfur world and the origins of life: abiotic synthesis from metallic iron, H_2S and CO_2: a comparison of the thiol generating $FeS/HCl(H_2S)/CO_2$-system and its $Fe^0/H_2S/CO_2$-counterpart. Proceedings Koninklijke Nederlandse Akademie van Wetenschappen, Amsterdam 100, pp 11–25
Helz GR, Miller CV, Charnock JM, Mosselmans JFW, Pattrick RAD, Garner CD, Vaughan DJ (1996) Mechanism of molybdenum removal from the sea and its concentration in black shales. EXAFS evidence. Geochim Cosmochim Acta 60: 3631–3642

Henderson-Sellers A, Henderson-Sellers B (1988) Equable climate in the early Archaean. Nature 336: 117–118

Hengeveld R (2007) Two approaches to the study of the origin of life. Acta Biotheor 55 (this issue). doi: 10.1007/s10441-007-9017-6

Hennet RJ-C, Holm NG, Engel MH (1992) Abiotic synthesis of amino acids under hydrothermal conditions and the origin of life: a perpetual phenomenon? Naturwissenschaften 79: 361–365

Herrera AL (1942) A new theory of the origin and nature of life. Science 96: 14

Hirsch AKH, Fischer FR, Diederich F (2007) Phosphate recognition in structural biology. Angew Chem (Int Ed Engl) 46:338–352

Hoskin PWO, Schaltegger U (2003) The composition of zircon and igneous and metamorphic petrogenesis, in Hanchar JM, Hoskin PWO, eds., Zircon: Min Soc America, Reviews in Mineralogy and Geochemistry 53:27–62

Hovland M (2002) On the self-sealing nature of marine seeps. Continental Shelf Res 22: 2387–2394

Huber C, Wächtershäuser G (1997) Activated acetic acid by carbon fixation on (Fe,Ni)S under primordial conditions. Science 276: 245–247

Huber C, Wächtershäuser G (1998) Peptides by activation of amino acids on (Fe,Ni)S surfaces: implications for the origin of life. Science 281:670–672

Huber C, Wächtershäuser G (2003) Primordial reductive amination revisited. Tetrahedron Lett 44: 1695–1697

Huber C, Wächtershäuser G (2006) α-hydroxy and α-amino acids under possible Hadean, volcanic origin-of-life conditions. Science 314:630–632

Huber C, Eisenreich W, Hecht S, Wächtershäuser G (2003) A possible primordial peptide cycle. Science 301: 938–940

Huntrieser H, Feigl C, Schlager H, Schröder F, Gerbig C, van Velthoven P, Flatøy F, Théry C, Petzold A, Höller H, Schumann U (2002) Airborne measurements of NO_x, tracer species, and small particles during the European Lightning Nitrogen Oxides Experiment. J Geophys Res 107:D11, 4113, 10.1029/2000JD000209

Janecky DR, Seyfried WE (1983) The solubility of magnesium-hydroxide-sulfate-hydrate in seawater at elevated temperatures and pressures. Am J Sci 283:831–860

Jaynes ET (1979) Where do we stand on maximum entropy? In: Levine RD, Tribus M (eds) The maximum entropy principle. MIT, Cambridge, MA, USA, pp 15–118

Jadhav VR, Yarus M (2002) Coenzymes as ribozymes. Biochimie 84:877–888

Johnston WK, Unrau PJ, Lawrence MS, Glasner ME, Bartel DP (2001) RNA-catalyzed RNA polymerization: accurate and general RNA-templated primer extension. Science 292:1319–1325

Jupp T and Schultz A (2000) A thermodynamic explanation for black smoker temperatures. Nature 403:880–883

Kakegawa T, Noda M, Nannri H (2002) Geochemical cycles of bio-essential elements on the early Earth and their relationships to the origin of life. Resour Geol 52: 83–89

Kappler A, Pasquero C, Konhauser KO, Newman DK (2005) Deposition of banded iron formations by anoxygenic phototrophic Fe(II)-oxidizing bacteria. Geology 33: 865–868

Kasting JF, Ackerman TP (1986) Climatic consequences of very high carbon dioxide levels in the earth's early atmosphere. Science 234:1383–1385

Kasting JF, Brown LL (1998) The early atmosphere as a source of biogenic compounds. In: Brack A (ed) The molecular origins of life. Cambridge University Press, Cambridge, pp 35–56

Kasting JF, Eggler DH, Raeburn SP (1993) Mantle redox evolution and the oxidation state of the Archean atmosphere. J Geol 101:245–257

Kasting JF, Zahnle KJ, Pinto JP, Young AT (1989) Sulfur, ultraviolet radiation, and the early evolution of life. Orig Life Evol Biosph 19: 95–108

Kasting JF, Howard MT, Wallmann K, Veizer J, Shields G, Jaffrés J (2006) Paleoclimates, ocean depth, and the oxygen isotopic composition of seawater. Earth Planet Sci Lett 252:82–93

Katona G, Carpentier P, Nivière V, Amara P, Adam V, Ohana J, Tsanov N, Bourgeois D (2007) Raman-assisted crystallography reveals end-on peroxide intermediates in a nonheme iron enzyme. Science 316: 449–453

Kazmierczak J, Altermann W (2002) Neoarchean biomineralization by benthic cyanobacteria. Science 298: 2351

Kell DB (1988) Protonmotive energy-transducing mechanisms: some physical principles and experimental approaches. In: Anthony C (ed) Bacterial energy transduction. Academic Press, London, pp 429–490

Kelley DS, Karson JA, Blackman DK et al (2001) An off-axis hydrothermal vent field near the Mid-Atlantic Ridge at 30° N. Nature 412:145–149
Kelley DS, Karson JA, Früh-Green GL et al. (2005) A serpentinite-hosted ecosystem: The Lost City Hydrothermal field. Science 307:1428–1434
Kempe S, Degens ET (1985) An early soda ocean? Chem Geol 53:95–108
Kempe S, Kazmierczak J, Degens ET (1989) The soda ocean concept and its bearing on biotic evolution. In: Crick RE (ed) Origin, evolution and modern aspects of biomineralization in plants and animals. Plenum Press, New York, pp 29–43
Kharecha P, Kasting J, Siefert J (2005) A coupled atmosphere–ecosystem model of the early Archean Earth. Geobiology 3:53–76
Kleidon A (2004) Beyond Gaia: thermodynamics of life and earth system functioning. Clim Change 66:271–319
Kleidon A, Lorenz RD (eds) (2005) Non-equilibrium thermodynamics and the production of entropy: life, Earth, and beyond. Springer Verlag, pp 260
Kling GW, Tuttle ML, Evans WC (1989) The evolution of thermal structure and water chemistry in Lake Nyos. J Volcanol Geotherm Res 39: 151–165
Knight RD, Landweber LF (1998) Rhyme or reason: RNA–arginine interactions and the genetic code. Chem Biol 5:215–220
Knight RD, Landweber LF (2000) The early evolution of the genetic code. Cell 101:569–572
Konhauser KO, Hamade T, Raiswell R, Morris RC, Ferris FG, Southam G, Canfield DE (2002) Could bacteria have formed the Precambrian banded iron formations? Geology 30: 1079–1082
Koonin EV, Martin W (2005) On the origin of genomes and cells within inorganic compartments. Trends Genet 21: 647–654
Krishnan M, Ugaz VM, Burns MA (2002) PCR in a Rayleigh-Bénard convection cell. Science 298:793
Krishnarao JSR (1964) Native nickel–iron alloy, its mode of occurrence, distribution and origin. Econ Geol 59: 443–448
Krupp RE (1994) Phase relations and phase transformations between low temperature iron sulfides mackinawite, greigite and smythite. Eur J Mineral 6: 389–396
Kuhn H, Kuhn C (2003) Diversified world: drive to life's origin. Angew Chem Int Ed 42:262–266
Kump LR, Seyfried WE (2005) Hydrothermal Fe fluxes during the Precambrian: effect of low oceanic sulfate concentrations and low hydrostatic pressure on the composition of black smokers. Earth Planet Sci Lett 235: 654–662
Kusakabe M, Tanyileke GZ, McCord SA, Schladow SG (2000) Recent pH and CO_2 profiles at Lakes Nyos and Monoun, Cameroon: implications for the degassing strategy and its numerical simulation. J Volcanol Geotherm Res 97:241–260
Lancaster JR (ed) (1988) The bioinorganic chemistry of nickel. VCH, Weinheim, Germany
Lane N (2004) Oxygen: the molecule the made the world. Oxford University Press, Oxford
Lawrence MS, Bartel DP (2003) Processivity of ribozyme catalyzed RNA polymerase. Biochemistry 42: 8748–8755
Lawrence MS, Bartel DP (2005) New ligase-derived RNA polymerase ribozymes. RNA 11:1173–1180
Leduc S (1911) The mechanism of life. Rebman Ltd, London
Leman L, Orgel L, Ghadiri MR (2004) Carbonyl sulfide-mediated prebiotic formation of peptides. Science 306:283–286
Lesher CM, Stone WE (1997) Exploration geochemistry of komatiites. In: Wyman DA (ed) Trace element geochemistry of volcanic rocks: applications for massive sulphide exploration, vol 12. Short Course Notes, Geological Society of Canada, pp 153–204
Lind J (1988) Hausmannite (Mn_3O_4) conversion to manganite (γ-MnOOH) in dilute oxalate. Environ Sci Technol 22:62–70
Liu SV, Zhou J, Zhang C, Cole DR, Gajdarziska-Josifovska M, Phelps TJ (1997) Thermophilic Fe(III)-reducing bacteria from the deep subsurface: the evolutionary implications. Science 277: 1106–1109
Loll B, Kern J, Saenger W, Zouni A, Biesiadka J (2005) Towards complete cofactor arrangement in the 3.0 Å resolution structure of photosystem II. Nature 438:1040–1044
Loreau M (1995) Consumers as maximizers of matter and energy flow in ecosystems. Am Nat 15: 237–240
Lorenz EN (1996) The essence of chaos. University of Washington Press, Seattle, WA
Lorenz R (2003) Full steam ahead—probably. Science 299: 837–838
Lorenz RD (2002) Planets, life and the production of entropy. Int J Astrobiol 1: 3–13
Lotka AJ (1945) The law of evolution as a maximal principle. Human Biol 17: 167–194

Lovelock J (1988) The ages of gaia. Oxford University Press, Oxford
Lovelock J (2001) Homage to gaia: the life of an independent scientist. Oxford University Press, Oxford
Lowell RP, Keller SM (2003) High-temperature seafloor hydrothermal circulation over geologic time and archean banded iron formations. Geophys Res Lett 30:1391. doi: 10.1029/2002GL016536
Ludwig KA, Kelley DS, Butterfield DA, Nelson BK, Früh-Green G (2006) Formation and evolution of carbonate chimneys at the Lost City hydrothermal field. Geochim Cosmochim Acta 70:3625–3645
Macleod G, McKeown C, Hall AJ, Russell MJ (1994) Hydrothermal and oceanic pH conditions of possible relevance to the origin of life. Orig Life Evol Biosph 24:19–41
Maden BEH (2000) Tetrahydrofolate and tetrahydromethanopterin compared: functionally distinct carriers in C1 metabolism. Biochem J 350: 609–629
Maisonneuve J (1982) The composition of the Precambrian ocean waters. Sediment Geol 31:1–11
Marshall WL (1994) Hydrothermal synthesis of amino acids. Geochim Cosmochim Acta 58: 2099–2106
Marteinsson VTh, Kristjánsson JK, Kristmannsdöttir H et al. (2001) Discovery of giant submarine smectite cones on the seafloor in Eyjafjordur, Northern Iceland, and a novel thermal microbial habitat. Appl Environ Microbiol 67:827–833
Martin W, Russell MJ (2003) On the origin of cells: an hypothesis for the evolutionary transitions from abiotic geochemistry to chemoautotrophic prokaryotes, and from prokaryotes to nucleated cells. Phil Trans Roy Soc Lond (Ser B) 358: 27–85
Martin W, Russell MJ (2007) On the origin of biochemistry at an alkaline hydrothermal vent. Phil Trans Roy Soc Lond (Ser.B), DOI 10.1098/rstb.2002.1183
Martin W, Rote C, Hoffmeister M, Theissen U, Gelius-Dietrich G, Ahr S, Henze K (2003) Early cell evolution, eukaryotes, anoxia, sulfide, fungi first (?), and a tree of genomes revisited. Life 55: 193–204
Maurette M, Brack A, Duprat J, Engrand C (2004) Delivery of micrometeoritic greenhouse gases and "smoke" particles during the post-lunar "late heavy bombardment" of the Earth. 35th COSPAR Scientific Assembly, 18–25 July, Abstract 04-A-02754, Paris
McCollom T, Seewald JS (2003) Experimental constraints on the hydrothermal reactivity of organic acids and acid anions. I. Formic acid and formate. Geochim Cosmochim Acta 67:3625–3644
Mehta MP, Baross JA (2006) Nitrogen fixation at 92°C by a hydrothermal vent archaeon. Science 314: 1783–1786
Mellersh AR (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. Orig Life Evol Biosph 23: 261–274
Mellersh AR, Wilkinson A-S (2000) RNA bound to a solid phase can select an amino acid and facilitate subsequent amide bond formation. Orig Life Evol Biosph 30:3–7
Mereschkowsky C (1910) Theorie der zwei Plasmaarten als Grundlage der Symbiogenesis, einer neuen Lehre von der Entstehung der Organismen. Biol Centralbl 30: 278–288; 289–303: 321–347; 353–367
Miller SR, Wingard CE, Castenholz RW (1998) Effects of visible light and UV radiation on photosynthesis in a population of a hot spring cyanobacterium, a *Synechococcus* sp., subjected to high-temperature stress. Appl Environ Microbiol 64:3893–3899
Milner-White EJ (1997) The partial charge of the nitrogen atom in peptide bonds. Protein Sci 6: 2477–2482
Milner-White EJ, Russell MJ (2005) Nests as sites for phosphates and iron–sulfur thiolates in the first membranes: 3 to 6 residue anion-binding motifs. Orig Life Evol Biosph 35: 19–27
Milner-White EJ, Nissink WM, Allen FH, Duddy WJ (2004) Recurring main chain anion-binding motifs in short polypeptides. Acta Crystallogr (Sect D) 60: 1935–1942
Mitchell P (1967) Proton-translocation phosphorylation in mitochondria, chloroplasts and bacteria: natural fuel cells and solar cells. Fed Am Soc Exp Biol 26:1370–1379
Mojzsis SJ, Harrison TM, Pidgeon RT (2001) Oxygen-isotope evidence from ancient zircons for liquid water at the earth's surface 4,300 Myr ago. Nature 409: 178–181
Moore PB, Steitz TA (2003) After the ribosome structures: how does peptidyl transferase work? RNA 9: 155–159
Morel FMM, Price NM (2003) The biogeochemical cycles of trace metals in the oceans. Science 300: 944–947
Morita RY (2000) Is H_2 the universal energy source for long-term survival? Microb Ecol 38: 307–320
Morowitz H, Smith E (2006) Energy flow and the organization of life. Santa Fé Special Paper #06–08–029
Morse JW, Arakaki T (1993) Adsorption and coprecipitation of divalent metals with mackinawite (FeS). Geochim Cosmochim Acta 57: 3635–3640

Morse JW, Mackenzie FT (1998) Hadean ocean carbonate geochemistry. Aquat Chem 4: 301–319
Moulton V, Gardner PP, Pointon RF, Creamer LK, Jameson GB, Penny D (2000) RNA folding argues against a hot origin of life. J Mol Evol 51:416–421
Mulkidjanian AY, Junge W (1997) On the origin of photosynthesis as inferred from sequence analysis? A primordial UV-protector as common ancestor of reaction centers and antenna proteins. Photosynth Res 51:27–42
Müller V (2003) Energy conservation in acetogenic bacteria. Appl Environ Microbiol, pp 6345–6353
Muth GW, Orteleva-Donnelly L, Strobel SA (2000) A single adenosine with a neutral pK_a in the ribosomal peptidyl transferase center. Science 289:947–950
Navarro-González R, McKay CP, Mvondo DN (2001) A possible nitrogen crisis for Archaean life due to reduced nitrogen fixation by lightning. Nature 412:61–64
Neal C, Stanger G (1984) Calcium and magnesium hydroxide precipitation from alkaline groundwater in Oman, and their significance to the process of serpentinization. Mineral Mag 48: 237–241
Nisbet EG, Sleep NH (2001) The habitat and nature of early life. Nature 409: 1083–1091
Nissen P, Hansen J, Muth GW, Ban N, Moore PB, Strobel SA, Steitz TA (2001) Mechanism of ribosomal peptide bond formation. Science 291: 203
Nissen P, Hansen J, Ban N, Moore PB, Steitz TA (2000) The structural basis of ribosome activity in peptide bond synthesis. Science 289: 920–930
Osborn HF (1917) The origin and evolution of life: on the theory of action, reaction and interaction of energy. Charles Scribner's Sons, New York
Ostro S, Russell MJ (in review) Nickel–iron micrometeorites at 4.4 Ga—grist to emergent life's mill
Pace NR (1997) A molecular view of microbial diversity and the biosphere. Science 276: 734–740
Pace NR (2002) The large scale topology of the tree of life. Abstract. Astrobiology 2: 484
Palandri JL, Reed MH (2004) Geochemical models of metasomatism in ultramafic systems: serpentinization, rodingitization, and sea floor carbonate chimney precipitation. Geochim Cosmochim Acta 68: 1115–1133
Pavlov AA, Toon OB, Pavlov AK, Bally J, Pollard D (2005) Passing through a giant molecular cloud: "Snowball" glaciations. Geophys Res Lett 32, L03705, doi:10.1029/2004GL021890
Penny D (2005) An interpretative review of the origin of life research. Biol Phil 20: 633–671
Phoenix VR, Konhauser KO, Adams DG, Bottrell SH (2001) Role of biomineralization as an ultraviolet shield: implications for Archean life. Geology 29: 823–826
Pontes-Buarque M, Tessis AC, Lopez AC, de Monte MBM, Bonapace JAP, Vieyra AR, Souza-Barros F (2001) Modulation of adenosine 5'-monophosphate adsorption onto aqueous resident pyrite: potential mechanisms for prebiotic reactions. Orig Life Evol Biosph 31: 343–362
Pratt JM (1993) Nature's design and use of catalysts based on Co and the macrocyclic corrin ligand: 4×10^9 years of coordination chemistry. Pure Appl Chem 65: 1513–1520
Proskurowski G, Lilley MD, Kelley DS, Olson EJ (2006) Low temperature volatile production at the Lost City Hydrothermal Field, evidence from a hydrogen stable isotope geothermometer. Chem Geol 229:331–343
Pullman B (1972) Electronic factors in biochemical evolution. In: Ponnamperuma C (ed) Exobiology. North Holland Publishing Company, Amsterdam, pp 136–169
Raymond J, Siefert JL, Staples CR, Blankenship RE (2004) The natural history of nitrogen fixation. Mol Biol Evol 21: 541–554
Reysenbach AL, Lovley DR (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 accepter. Int J Syst Evol Microbiol 52:719–728
Rickard D, Morse JW (2005) Acid volatile sulfide (AVS). Mar Chem 97: 141–197
Rickard D, Butler IB, Olroyd A (2001) A novel iron sulphide switch and its implications for earth and planetary science. Earth Planet Sci Lett 189: 85–91
Robert F, Chaussidon M (2006) A palaeotemperature curve for the Precambrian oceans based on silicon isotopes in cherts. Nature 443: 969–972
Roche Applied Science (1992) Biochemical pathways: Roche Diagnostics GmbH, Mannheim
Rosing MT, Frei R (2004) U-rich Archaean sea-floor sediments from Greenland—indications of $>$ 3700 Ma oxygenic photosynthesis. Earth Planet Sci Lett 217: 237–244
Rosing MT, Bird DK, Sleep NH, Glassley W, Albarede F (2006) The rise of continents—an essay on the geologic consequences of photosynthesis. Palaeogeogr Palaeoclimatol Palaeoecol 232: 99–113

Rouse RC, Peacor DR, Freed RL (1988) Pyrophosphate groups in the structure of canaphite, $CaNa_2P_2O_7.4H_2O$: the first occurrence of a condensed phosphate as a mineral. Am Mineral 73:168–171

Russell MJ (1995) The generation at hot springs of sedimentary ore deposits, microbialites and life. Ore Geol Rev 10:199–214

Russell MJ (2002) From the Journeywork of the Stars to the Wealth of Nations: A Refrain. In: Loose G, Brown J, Russell M (eds) (Conveners) Glasgow Poetry Festival

Russell MJ (2003) On the importance of being alkaline. Science 302: 580–581

Russell MJ, Skauli H (1991) A history of theoretical developments in carbonate-hosted base metal deposits and a new tri-level enthalpy classification. Econ Geol Monogr 8:96–116

Russell MJ, Arndt NT (2005) Geodynamic and metabolic cycles in the Hadean. Biogeosciences 2: 97–111

Russell MJ, Hall AJ (1997) The emergence of life from iron monosulphide bubbles at a submarine hydrothermal redox and pH front. J Geol Soc Lond 154: 377–402

Russell MJ, Hall AJ (2002) From geochemistry to biochemistry: chemiosmotic coupling and transition element clusters in the onset of life and photosynthesis. Geochem News 113:6–12

Russell MJ, Hall AJ (2006) The onset and early evolution of life. In: Kesler SE and Ohmoto H (eds) Evolution of early earth's atmosphere, hydrosphere, and biosphere—constraints from ore deposits. Geological Society of America, Memoir, vol 198, pp 1–32

Russell MJ, Martin W (2004) The rocky roots of the acetyl-CoA pathway. Trends Biochem Sci 29: 358–363

Russell MJ, Daia DE, Hall AJ (1998) The emergence of life from FeS bubbles at alkaline hot springs in an acid ocean. In: Wiegel J, Adams MWW (eds), Thermophiles: The keys to molecular evolution and the origin of life. Taylor & Francis, Washington, pp 77–126

Russell MJ, Daniel RM, Hall AJ, Sherringham J (1994) A hydrothermally precipitated catalytic iron sulphide membrane as a first step toward life. J Mol Evol 39:231–243

Russell MJ, Hall AJ, Cairns-Smith AG, Braterman PS (1988) Submarine hot springs and the origin of life. Nature 336:117

Russell MJ, Hall AJ, Turner D (1989) In vitro growth of iron sulphide chimneys: possible culture chambers for origin-of-life experiments. Terra Nova 1:238–241

Russell MJ, Hall AJ, Mellersh AR (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. Kluwer Academic Publishers, Dordrecht, pp 325–388

Russell MJ, Hall AJ, Fallick AE and Boyce AJ (2005) On hydrothermal convection systems and the emergence of life. Econ Geol 100: 419–438

Sanchez RA, Ferris JP and Orgel LE (1967) Studies in prebiotic synthesis II. Synthesis of purine precursors and amino acids from aqueous hydrogen cyanide. J Mol Biol 30: 223–253

Sánchez-Baracaldo P, Haye PK and Blank CE (2005) Morphological and habitat evolution in the cyanobacteria using a compartmentalization approach. Geobiology 3: 145–165

Sandiford M, McLaren S (2002) Tectonic feedback and the ordering of heat producing elements within the continental lithosphere. Earth Planet Sci Lett 204: 133–150

Sauer K, Yachandra VK (2004) The water-oxidation complex in photosynthesis. Biochim Biophys Acta Bioenerg 1655:140–148

Schaefer L, Fegley B (2007) Outgassing of ordinary chondritic material and some of its implications for the chemistry of asteroids, planets, and satellites. Icarus 186:462–483

Schönheit P, Schäfer T (1995) Metabolism of hyperthermophiles. World J Microbiol Biotechnol 11:26–57

Schoonen MAA, Xu Y, Bebie J (1999) Energetics and kinetics of the prebiotic synthesis of simple organic and amino acids with the $FeS-H_2/FeS_2$ redox couple as reductant. Orig Life Evol Biosph 29: 5–32

Schrödinger E (1944) What is life? The physical aspects of the living cell. Cambridge University Press, Cambridge

Schulte MD, Rogers KL (2004) Thiols in hydrothermal solution: standard partial molar properties and their role in the organic geochemistry of hydrothermal environments. Geochim Cosmochim Acta 68: 1087–1097

Schwartzman D, Lineweaver CH (2005) Temperature, biogenesis and biospheric self-organization. In: Kleidon A, Lorenz R (eds), Non-equilibrium thermodynamics and the production of entropy: life, earth and beyond. Springer Verlag, Berlin, pp 207–217

Seefeldt LC, Dance IG, Dennis RD (2004) Substrate interactions with nitrogenase: Fe versus Mo. Biochemistry 43:1401–1409

Seewald JS, Zolotov MY, McCollom T (2006) Experimental investigation of single carbon compounds under hydrothermal conditions. Geochim Cosmochim Acta 70:446–460

Seyfried WM, Bischoff JL (1981) Experimental seawater-basalt interaction at 300°C, 500 bars: chemical exchange, secondary mineral formation, and implications for transport of heavy metals. Geochim Cosmochim Acta 45: 135–147

Shen Y, Buick R (2004) The antiquity of microbial sulfate reduction. Earth-Sci Rev 64:243–272

Shock EL (1990) Geochemical constraints on the origin of organic compounds in hydrothermal systems. Orig Life Evol Biosph 20: 331–367

Shock EL (1992) Chemical environments of submarine hydrothermal systems. Orig Life Evol Biosph 22: 67–107

Shock E (1995) Organic acids in hydrothermal solution: standard molal thermodynamic properties of carboxylic acids and estimates of dissociation constants at high temperatures and pressures. Am J Sci 295:496–580

Shock EL, McCollom T, Schulte MD (1998) The emergence of metabolism from within hydrothermal systems. In Wiegel J, Adams MWW (eds) Thermophiles: the keys to molecular evolution and the origin of life. Taylor & Francis, Washington, pp 59–76

Sigurdsson H, Devine JD, Tchoua FM, Presser TS, Pringle MKW, Evans WC (1987) Origin of the lethal gas burst from Lake Monoun, Cameroon. J Volcanol Geotherm Res 31:1–16

Sleep NH, Zahnle K, Neuhoff PS (2001) Initiation of clement surface conditions on the early Earth. Proc Natl Acad Sci USA 98: 3666–3672

Sleep NH, Meibom A, Fridriksson Th, Coleman RG, Bird DK (2004) H_2-rich fluids from serpentinization. Geochemical and biotic implications. Proc Natl Acad Sci USA 101:12818–12823

Smith A (1776) An inquiry into the nature and causes of the wealth of nations. W. Strahan and T. Cadell, Edinburgh

Smolin L (1997) The life of the cosmos. Weidenfeld & Nicolson, London

Sowerby SJ, Heckl WM (1998) The role of self-assembled monolayers of the purine and pyridine bases in the emergence of life. Orig Life Evol Biosph 28:283–310

Sukumaran PV (2000) Evolution of the atmosphere and the oceans: evidence from the geological record. Resonance 5:4–12

Svetlitchnyi V, Dobbeck H, Meyer-Klaucke W, Meins T, Thiele B, Römer P, Huber R, Meyer O (2004) A functional Ni-Ni-[4Fe4S] cluster in the monomeric acetyl-CoA synthase from *Carboxydothermus hydrogenoformans*. Proc Natl Acad Sci USA 101:446–451

Swenson R (1989) Emergent attractors and the law of maximum entropy production: foundations to a theory of general evolution. Syst Res 6: 187–197

Swenson R (1997) Autocatakinetics, evolution, and the law of maximum entropy production: a principled foundation towards the study of human ecology. Adv Human Ecol 6: 1–47

Tamaura Y, Tabata M (1990) Complete reduction of carbon dioxide to carbon using cation-excess magnetite. Nature 346: 255–256

Tarasow TM, Tarasow SL, Eaton BE (1997) RNA-catalysed carbon–carbon bond formation. Nature 389: 54–57

Taylor P, Rummery TE, Owen DG (1979) Reactions of iron monosulfide solids with aqueous hydrogen sulfide up to 160°C. J Inorg Nucl Chem 41:1683–1687

Tessis AC, Penteado-Fava A, Pontes-Buarques M, de Amorim HS, Bonapace JAP, de Souza-Barros F, Monte MBM, Vieyra A (1999) Pyrite suspended in artificial sea water catalyzes hydrolysis of adsorbed ATP: enhancing effect of acetate. Origins Life Evol Biosph 29:361–374

Thauer RK (1998) Biochemistry of methanogenesis: a tribute to Marjory Stephensen. Microbiology (Amsterdam) 144: 2377–2406

Thauer RK, Jungermann K, Decker K (1977) Energy conservation in chemotrophic anaerobic bacteria. Bacteriol Rev 41: 100–180

Tice MM, Lowe DR (2006) Hydrogen-based carbon fixation in the earliest known photosynthetic organisms. Geology 34: 37–40

Trincher KS (1965) Biology and information: elements of biological thermodynamics. Consultants Bureau, New York

Tsukiji S, Pattnaik SB, Suga H (2004) Reduction of an aldehyde by a NADH/Zn^{2+}-dependent redox active ribozyme. J Am Chem Soc 126:5044–5045

Tyryshkin AM, Watt RK, Baranov SV, Dasgupta J, Hendrich MP, Dismukes GC (2006) Spectroscopic evidence for Ca^{2+} involvement in the assembly of the Mn_4Ca cluster in the photosynthetic water-oxidizing complex. Biochem 45:12876–12889

Ueno Y, Maruyama S, Isozaki Y, Yurimoto H (2001) Early Archean (ca. 3.5 Ga) microfossils and ^{13}C-depleted carbonaceous matter in the North Pole area, Western Australia: Field occurrence and geochemistry. In: Nakashima S, Marayuma S, Brack A, Windley BF (eds) Geochemistry and the origin of life. Universal Academy Press Inc., Tokyo, pp 203–236

Unrau PJ, Bartel DP (1998) RNA-catalysed nucleotide synthesis. Nature 395:260–263

Vaughan DJ, Craig JR (1978) Mineral chemistry of metal sulfides. Cambridge University Press, Cambridge

Vaughan DJ, Ridout MS (1971) Mössbauer studies of some sulfide minerals. J Inorg Nucl Chem 33: 741–747

Vladimirov MG, Ryzhkov YF, Alekseev VA, Bogdanovskaya VA, Otroshchenko VA, Kritsky MS (2004) Electrochemical reduction of carbon dioxide on pyrite as a pathway for abiogenic formation of organic molecules. Orig Life Evol Biosph 34:347–360

Volbeda A, Fontecilla-Camps JC (2005a) Structure-function relationships of nickel–iron sites in hydrogenase and a comparison with the active sites of other nickel–iron enzymes. Coord Chem Rev 249:1609–1619

Volbeda A, Fontecilla-Camps JC (2005b) Structural bases for the catalytic mechanism of Ni-containing carbon monoxide dehydrogenases. Dalton Trans 2005:3443 – 3450

von Neumann J (1951) The general and logical theory of automata. In: Jeffress LA (ed) Cerebral mechanisms in behavior—The Hixon Symposium. Wiley, New York, pp 1–31

Wächtershäuser G (1988a) Pyrite formation, the first energy source for life: a hypothesis. Syst Appl Microbiol 10:207–210

Wächtershäuser G (1988b) Before enzymes and templates: theory of surface metabolism. Microbiol Rev 52: 452–484

Wächtershäuser G (1990) Evolution of the first metabolic cycles. Proc Natl Acad Sci USA 87:200–204

Wächtershäuser G (2006) From volcanic origins of chemoautotrophic life to Bacteria, Archaea and Eukarya. Phil Trans Roy Soc Lond (Ser B) 361: 1787–1808

Walker JCG (1985) Carbon dioxide on the early Earth. Orig Life Evol Biosph 16: 117–127

Watson JD, Milner-White EJ (2002) A novel main chain anion-binding site in proteins: the nest. A particular combination of ϕ,Ψ values in successive residues gives rise to anion-binding sites that occur commonly and are found often at functionally important regions. J Mol Biol 315:171–182

Wenner DB, Taylor HP (1971) Temperatures of serpentinization of ultramafic rocks based on $^{18}O/^{16}O$ fractionation between coexisting serpentine and magnetite. Contrib Mineral Petrol 32:165–185

Westall F (2004) Early life on earth: the fossil record. In: Ehrenfreund P et al. (eds), Astrobiology: future perspectives. Kluwer, Dordrecht, pp 287–316

Westall F, de Witt MJ, Dann J, Van der Gaast S, de Ronde C, Gerneke R (2001) Early Archean fossil bacteria and biofilms in hydrothermally influenced sediments from the Barberton Greenstone Belt, South Africa. Precambrian Res 106: 93–116

White HB (1976) Coenzymes as fossils of an earlier metabolic state. J Mol Evol 7:101–104

Whitman W (1900) Leaves of grass. David McKay, Philadelphia

Whitman WB, Coleman DC, Wiebe WJ (1998) Prokaryotes: the unseen majority. Proc Natl Acad Sci USA 95:6578–6583

Wicken JS (1988) Evolution, information and thermodynamics: extending the Darwinian program. Oxford University Press, New York

Wilde SA, Valley JW, Peck WH, Graham CM (2001) Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago. Nature 409:175–178

Williams RJP, Frausto da Silva JJR (2003) Evolution was chemically constrained. J Theor Biol 220: 323–343

Woese CR, Dugre DH, Saxinger WC, Dugre SA (1966) The molecular basis for the genetic code. Proc Natl Acad Sci USA 55:966–974

Wolin MJ (1982) Hydrogen transfer in microbial communities. In: Bull AT, Slater JH (eds) Microbial interactions and communities. Academic Press, London

Wolthers M, Van der Gaast SJ, Rickard D (2003) The structure of disordered mackinawite. Am Mineral 88:2007–2015

Wood BJ, Halliday AN (2005) Cooling of the Earth and core formation after the giant impact. Nature 437:1345–1348

Yamagata Y, Wanatabe H, Saitoh M, Namba T (1991) Volcanic production of polyphosphates and its relevance to prebiotic evolution. Nature 352: 516–519

Yano J, Kern J, Sauer K, Latimer MJ, Pushkar Y, Biesiadka J, Loll B, Saenger W, Messinger J, Zouni A, Yachandra VK (2006) Where water is oxidized to dioxygen: Structure of the photosynthetic Mn_4Ca cluster. Science 314:821–825

Yarus M (1988) A specific amino acid binding site composed of RNA. Science 240:1751–1758

Yarus M (1989) Specificity of arginine binding by the *Tetrahymena* intron. J Mol Evol 28:980–988

Yarus M (1998) Amino acids as RNA ligands: a direct-RNA-template theory for the code's origin. J Mol Evol 47:109–117

Yarus M (2000) RNA-ligand chemistry: a testable source for the genetic code. RNA 6:474–484

Yarus M, Caporaso JG, Knight R (2005) Origins of the genetic code: the escaped triplet theory. Ann Rev Biochem 74:179–198

Zhang B, Cech TR (1997) Peptide bond formation by in vitro selected ribozymes. Nature 390:96–100

Zhang S, Holmes T, Lockshin C, Rich A (1993) Spontnaneous assembly of a self-complementary oligopeptide to form a stable macroscopic membrane. Proc Natl Acad Sci USA 90:3334–3338

Zhang Z, Satpathy S (1991) Electron states, magnetism, and the Verwey transition in magnetite. Phys Rev B 44:13319–13331

Zou W, Ibrahem I, Dziedzic P, Sundén H, Córdova A (2005) Small peptides as modular catalysts for the direct asymmetric aldol reaction: ancient peptides with aldolase enzyme activity. Chem Commun 2005:4946–4948