Some Molecular Moments of the Hadean and Archaean Aeons: A Retrospective Overview from the Interfacing Years of the Second to Third Millennia

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1. Introduction—Our Embryonic Universe

The practice of physics and chemistry—the making and breaking of molecular bonds arising from the interactions of matter and energy—is coincidental with the earliest matter/energy of the Cosmos. From this primordial plasma—the hot dense soup of subatomic particles that filled the early universe—electrons and protons first combined to form hydrogen atoms.[1] Based on the Cold Dark Matter (CDM) model of cosmic events, the luminosity of this very early Universe[2] may have arisen from galaxies and quasars—among its oldest known objects (a quasar forms inside a galaxy that lies at the center of a massive dark matter halo). These complexes are powered by infalling gas, which, responding to their gravitational pull, impacts on the galactic gas, generating a strong accretion shock, characterized by a prodigious outpouring of energy, while falling into black holes at their centers. If the distinct spectral signature involving Lyman α (alpha) absorption by intergalactic hydrogen that is partially ionized by the radiation produced by a quasar is confirmed, it would provide the first observational evidence that quasars are embedded in great halos of dark matter.[3]

Spectral evidence from the most distant quasar currently known (SSJ1148+5251) points to two distinct phases of reionization in the Universe. Since the most important effect that formation of stars had on their environment is the reionization of the gas in the Universe, the radiation from the first generation of massive luminous stars and their eventual explosion as supernovae could have disrupted further star formation in their vicinity, leading to a hiatus during which ionized gas in the Universe might have recombined to become neutral again. A later generation of stars in young galaxies and quasars might have completed the reionization at the end of the cosmic Dark Ages, when the Universe was about a billion years old.[4]

Our Cosmos's first protogalaxies are thought to have coalesced at the higher density nodes in the filamentous network of this early cosmic structure. Within these protogalaxies, the denser regions of gas collapsed to form the first stars.[5] Within this atmosphere, or interstellar medium (ISM),

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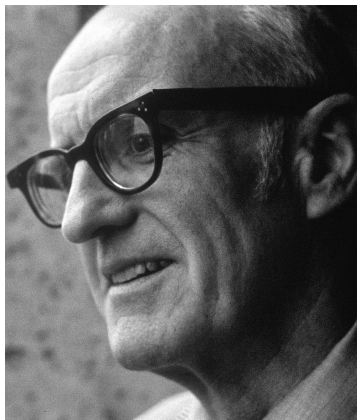
E. T. McGuinness pursued his academic degrees in chemistry at St. Peter's College (B.S.), Fordham (M.S.), and Rutgers (Ph.D.) Universities. These studies were interspersed with industrial laboratory experience in the pharmaceutical and fermentation industries prior to joining the faculty of Chemistry and Biochemistry at Seton Hall University in 1955. The main thrust of his research interests with graduate and undergraduate students was directed to mechanistic aspects of various enzymes, among them, aldose reductase, sorbitol and mannitol dehydrogenase, and NAD kinase. He moved to emeritus status in 1997.

the light elements Li, Be, and B were created by high-energy cosmic ray or neutrino spallation reactions on the target nuclei C, N, and O. All other elements ($6 \leq Z \leq 30$) and ($Z > 30$) owe their existence to nuclear (fusion) reactions in stellar interiors.[6] When stars exhaust their nuclear fuel and die, those at least as massive as the Sun expel much of their matter back into the ISM. Thus, each generation of stars pollutes the medium with the heavier elements of stellar nucleosynthesis.[7] A low-mass star, with an extremely low iron abundance and a striking excess of C and N, discovered within the Galactic halo[8] may be but the first among many.[9] Such a population of stars, formed from gas of low-metal content, could prove to be among the most ancient in the Universe, affording us a view of the makeup of the ISM of that time, >12 Gya (1 Gya = 10^9 years ago) before the present time.

Scattered within the ISM are regions known as clouds (ISCs) of varying densities which may be light years in extent and contain material in the form of both gas and small dust particles.[10] Spectral probes with different sources of electromagnetic radiation reveal that elemental abundances, which are mainly atomic and neutral, resemble those in stars, with H and He dominating (H ≫ He ≫ O > C, N). Many unidentified adsorption bands are thought to be caused by large and exotic organic molecules in the gas. Within large dense ISCs (stellar birthplaces), gaseous matter is known to be overwhelmingly molecular. The dust particles, or grains, would appear to be of two populations—one carbonaceous and the other composed of metallic silicates. Broad adsorption bands are caused by ice mantles of H_2O, CO, CO_2, and CH_3OH that develop around dust particle cores.[11] The main effects of dust particles are these: dust extinguishes starlight and provides a surface on which molecules may freeze out and on which chemistry may occur.[12] The putative presence of the carbon trioxide (CO_3) molecule in these low-temperature ices and on Mars might be responsible for the presence of an ^{18}O enrichment in Earth and Mars atmospheric CO_2.[13] The environment of these dense ISCs, where the greatest number and variety of molecules are found, is characterized by a temperature of 10−50 K, a relatively high density of particulate matter ($\sim$1 m^{-3}!), and a molecular

density that is significantly greater ($\sim10^4$ molecules cm^{-3}) than the average molecular density ($\sim$1 molecules cm^{-3}) throughout the ISM. The grains provide a catalytic surface, or platform, for the transformation, $2H \rightarrow H_2$, the most abundant molecule in the ISCs. The majority of molecules are electrically neutral, many are highly unsaturated, some are free radicals, and others are ions (Figure 1).

Given the thermodynamic and kinetic barriers to be expected, the demonstration that chemical reactions between electrically neutral species can be extremely rapid in this milieu tells us that it is a different kind of chemistry from that found on Earth.[14] Spectroscopic and other observations have clearly demonstrated that solid-state compounds of both organic and inorganic nature are produced in abundance in the circumstellar envelopes of evolved stars over very short ($\sim10^3$ year) time scales during the last stages of stellar evolution.[15] Previously unidentified spectroscopic bands associated with gas and dust, and found throughout the galaxy, are attributed to the presence of polycyclic aromatic hydrocarbons, PAHs, fullerenes, and C_6H^-, the hexatriyne anion.[16]

Models of steady-state gas-phase interstellar chemistry and observations of interstellar N_2H^+ predict N_2 should be the most abundant nitrogen-bearing molecule in the interstellar medium. Recent observations using far-ultraviolet wavelengths toward HD 124314, a star in the Centaurus constellation, point to a disparity of the N_2 fractional abundance distribution between diffuse and dense molecular clouds, suggesting that current models of N_2 chemistry in the interstellar medium are incomplete and need to be rethought.[17]

A rich brew of molecular interactions occurring primarily in massive, dense clouds is initiated by primary processes (cosmic ray ionization of H_2 and He) to generate H_2^+ and He^+

$$\text{(a) } H_2 - h\nu \rightarrow H_2^+; \quad \text{(b) } He - h\nu \rightarrow He^+ \quad (1)$$
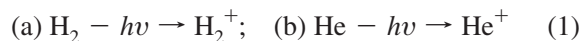
Given the lack of H_2 reactivity with He^+, the latter ion species is available to trigger a secondary process—the copious production of carbon ions by the reaction

$$He^+ + CO \rightarrow C^+ + O + He \quad (2)$$

C^+ adds efficiently to existing organic species, thereby increasing their carbon-chain length and producing an interesting organic-rich molecular universe. In H_2-dominated plasmas, the molecular ion, H_3^+, a fundamental constituent of interstellar chemistry, is produced easily by the rapid ion-neutral reaction

$$H_2 + H_2^+ \rightarrow H_3^+ + H \quad (3)$$
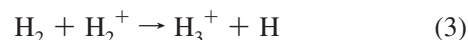
H_3^+ in turn reacts efficiently with almost any neutral atom or molecule, e.g.,

$$H_3^+ + CO \rightarrow H_2 + HCO^+ \quad (4)$$

to initiate a network of ion-neutral reactions, generating molecules such as OH, CO, CH_4, and H_2O.[18]

Viewed from a cosmic perspective, the totality of ordinary (baryonic) matter (e.g., electrons, neutrons, protons in the ISM, ISCs, stars, circumstellar gas, planets, all living entities) contributes only $\sim$4% of the total energy density of the Universe.[19] Some baryons, long thought to be "missing", may

Figure 1. Adapted with permission from ref 14a. Copyright 2002 American Chemical Society.
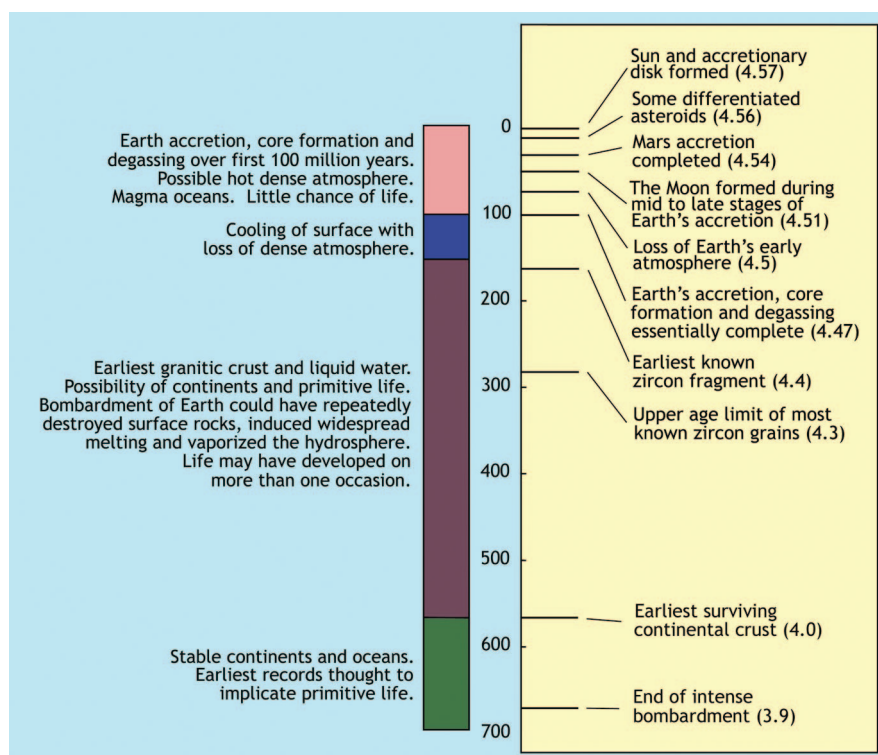
Figure 2. Earth's earliest history, in millions of years, starting from the origin of the Solar System; numbers on the right show absolute ages in billions of years. Dynamic modeling, U−Pb dating of meteorites, and the use of short-lived nuclides all provide evidence for how the Earth formed over the first 100 million years of the Solar System's existence. The Dark Ages of before 4 billion years ago, strictly termed the Hadean, is a period from which no rocks seem to have survived. All we have from this time are a few zircon grains. Wilde et al. (2001)[39b] and Mojzsis et al. (2001)[39a] are the latest to show that zircons nonetheless represent a wonderful archive of information about the early Earth. Adapted with permission from ref 27. Copyright Macmillan Publishers Ltd., *Nature*, 2001.

be distributed in highly ionized gas clouds encompassing the entire Local Group of galaxies.[20] The radiative contributions (e.g., photons, cosmic microwave background, CMB) amount to ~0.005%. The dominant energy density contributors are dark matter[21] and dark energy.[22] Galaxies and clusters of galaxies are gravitationally held together by vast halos of dark (i.e., nonluminous) matter.[23] The expressions "dark matter" and "dark energy" serve mainly to convey our present lack of detailed understanding concerning their makeup.[24] The recent discovery that the CMB radiation

permeating the Cosmos is partially polarized[25] opens up a whole new window of discovery on this early Universe.[26]

Here, against this encapsulated background, we draw on some recent developments culled from the subdisciplines of physics, chemistry, and biology, with emphasis focused on the years (from 1997 to late 2007) interfacing the second to third millennia, and investigations that shed retrospective light on aspects of Earth's molecular infancy (Figure 2), from the Hadean Aeon (>4.0 Gya)[27] to the rise of oxygen in the Archaean Aeon (~2.1 Gya). Since disciplinary origins and

affiliations have tended to merge and are no longer readily identifiable,[28] the focus in this review is directed more to molecule and molecule−ion interactions themselves and less to the discipline of conventional affiliation, except for purposes of clarity.

2. A Beginning: Some Physics/Chemistry and the Birth of Earth

2.1. Early to Middle Hadean

The Allende meteorite which fell to Earth in Mexico in 1969 continues to give up its secrets concerning the origin of our Sun and its planetary embryos. From recent studies on its Fe- and Mg-silicate spherules (chondrules) and Ca- and Al-rich inclusions (CAIs), new evidence has been gleaned demonstrating the presence of large ^{26}Mg excesses arising from the *in situ* decay of ^{26}Al (^{26}Al (∼730,000 year) → ^{26}Mg) in its chondrules and CAIs. This excess of the daughter isotope is taken to mean that the meteorite material once contained ^{26}Al. CAIs are the earliest objects yet identified that bear clear isotopic evidence of having been formed inside the Solar System.[29] Some ∼4.6 Gya, our inner Solar System must have seen episodic fiery rain showers of molten chondrules that lasted for ∼1 × 10⁶ years or more, generated by shock fronts originating from spiraling arms in the solar nebula.[30]

Earth's earliest accretion may have been due to the cumulative contributions of space dust (possibly originating from the Kuiper belt and Oort cloud of our Solar System[31] plus cometary and meteorite impactions).[32] Some feel for the origins and complex chemistry of interstellar dust grains, and primitive meteorites can be gained from a study of Mo isotope anomalies in carbonaceous chondrites.[33] Recent discoveries point to the fact that the Kuiper belt may be a reservoir of bodies considered to be primordial remnants of the nascent solar system.[34] Near infrared observations of Quaoar, the largest and brightest known Kuiper belt object, reveal the presence of crystalline ice and ammonia hydrate, pointing to past evidence of cryovolcanic outgassing and/or impact exposure of previously buried ices.[35]

During its prebiotic period, Earth accreted copious amounts of abiotic matter, much of it settling to the surface within small interplanetary dust particles (IDPs), or from silicate grains with some components from each source showing evidence of presolar origin.[36] (As noted below, valuable information on planetary gestation can be extracted by isotopic analyses of these grains.) Samples of particles in the upper atmosphere, possibly of cometary origin, snagged by high-flying aircraft were found to contain as much as 50% carbon, most tied up in kerogen, with some as polycyclic aromatic hydrocarbons (PAHs). Although composed mostly of metal/rock, some impacted asteroid fragments (meteorites) displayed evidence of complex organic molecules, including carboxylic acids, ketones, amines, amides, and quinones. A detailed statistical model has been proposed to account for the suite of processes involved in the transport of small asteroid fragments to Earth.[37] Since considerable amounts of galactic C, N, and O are tied up in large interstellar polymers, it is evident that planets such as ours start life with a significant "soup" of complex organic molecules in their inventory.[38]

2.2. Planetary Gestation: The Long and the Short of It

The Long

One scenario for the main features of our Planet's early development, based on work derived from $^{207}Pb/^{206}Pb$ and oxygen isotope measurements on zircon grains,[39] depicts Earth's growth as protracted and dominated by planetoid collisions,[40] reaching its present mass with a core of molten Fe and dissolved hydrogen.[41] Os/Re isotope analyses argue to an inner core formed to its present size within the first ∼250 million years after Earth's formation.[42] Earth's solid inner core is predominantly iron, but available data indicate the presence of oxygen and sulfur among others in the liquid outer core.[43] Intense meteor bombardment might have melted a considerable depth of the fledgling planets' rocky surfaces, giving rise to oceans of magma.[44] With a rudimentary atmosphere (∼4.47−4.51 Gya) and a sun some 25−30% less luminous,[45] subsequent cooling gave rise to a light continental crust by ∼4.3 or 4.4 Gya[46] and an anoxic ocean ∼4.3 Gya.[47]

The lower mantle (below ∼660 km) is thought to be dominated (70−80% by weight) by a dense magnesium−iron silicate, $(Mg,Fe,Al)(Si,Al)O_3$, with a stable "perovskite" crystal structure. Simulation experiments using magnesium perovskite and metallic iron and mimicking the high temperature−pressure synthesis conditions of the uppermost lower mantle demonstrated that the Fe^{3+} content of their perovskite is independent of the partial pressure of O_2; that is, low oxygen content is no barrier to iron oxidation.[48] The most realistic scenario is for O_2 to be provided by the disproportionation reaction

$$3FeO \rightarrow Fe + Fe_2O_3 \qquad (5)$$

The mantle's oxidation state is quantified in terms of relative oxygen fugacity ($\Delta \log fO_2$). Recent studies suggest that stable iron isotopes of mantle minerals can provide an independent means of estimating this parameter, complementing existing methods.[49]

The lowermost portion of this mantle, that segment extending some 200−300 km downward to the outer core−mantle boundary, is known as the D″ layer or discontinuity. Using experimental,[50] *ab initio*,[51] and a combination[52] of these approaches, simulating D″ layer conditions of temperature, pressure, and depth applied to $MgSiO_3$ perovskite, a profound transformation was found to occur in the crystalline structure of this mineral to a new high-pressure form, a "postperovskite phase". It was noted[53] that $(Mg_{0.9}, Fe_{0.1})SiO_3$ undergoes two such transitions, the second of which accords with the results of Murakami's group (125 GPa, 2500 K, ∼2700 km deep). A tendency for the layers of the postperovskite phase to align parallel to Earth's core in this D″ discontinuity can help explain the faster propagation of horizontally polarized (ν_{SH}) than vertically polarized (ν_{SV}) shear waves.[54]

Along parallel lines, magnesite ($MgCO_3$), the major component of subducted carbonates, when subjected to temperatures of 2100−2200 K and pressures above ∼115 GPa (∼2600 km depth), is transformed into a high-pressure form (magnesite II), where it may serve as a major host for oxidized carbon in the D″ layer.[55] Several phase relations of $MgCO_3$ in the deep mantle might include (i) some incorporation of carbon into the iron core, i.e.,

$$MgCO_3 \text{ (magnesite II)} + 5Fe \leftrightarrow Fe_3C + 2FeO + MgO \tag{6}$$
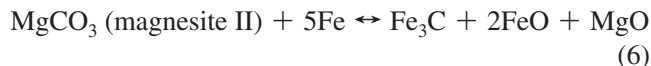
or (ii) magnesite II decomposition,

$$MgCO_3 \rightarrow MgO + CO_2 \tag{7}$$

in the D″ region associated with formation of a thermal boundary layer between the silicate mantle and the Fe-dominant core. Core−mantle reactions could further enrich the iron content in the D″ layer, given the unlimited reservoir of iron in the liquid core.[56] The higher Fe/Mn ratios of Hawaiian lavas relative to midocean ridge basalts (which only tap the upper mantle) reportedly point to the liquid Fe core as the source of this enhancement.[57] Clearly, a new era in the study of Earth's deepest mantle has begun.[58]

... and the Short of It

Experimental data relating to the origins of some of our Solar System's various components can be gleaned from records of now-extinct short-lived (radioactive) isotopes (e.g., ^{10}Be, ^{26}Al, ^{41}Ca) in chondritic meteorites.[59] Of particular interest from this class of nuclides, the ^{182}Hf ($t_{1/2} = 9 \times 10^6$ year) $\rightarrow ^{182}$W decay scheme provides a valuable chronometer for dating core formation in planetary bodies, based on the propensity of W to accumulate in the molten Fe core while Hf is retained in the silicate mantle. A revised model of this Hf $\rightarrow$ W decay scheme indicates that a rapid accretion and early core formation in the terrestrial planets, Earth and Mars, the asteroid Vesta, and Earth's Moon must have occurred during the first $\sim 30−34 \times 10^6$ years of the life of the Solar System, with a relatively short time span ($\sim 10 \times 10^6$ year) for the main growth stage of terrestrial planet formation.[60] The most significant differentiation event in the history of the Earth and other terrestrial planets was the separation of metal and silicate to form a metallic Fe-rich core and a silicate mantle.[61] At this point it is evident that we need a better knowledge of the processes that govern deep-Earth history[62] and the material parameters that control these processes before any kind of "standard model" can be constructed.[63]

A reinterpretation of the requisite target−impactor masses and angular momentum that led to the formation of the moon places this event near the very end of Earth's accumulation.[64] Giant impact simulations generate most of the Moon's mass from the silicate portion of the proto-planet Theia. The similarity in oxygen isotopes provides evidence that proto-earth and Theia were made from the same mix of materials[65] with more than 80% of the Moon's composition derived from impactor mantle material.[66] Theoretical simulations of proto-planetary gaseous disks, using 3-D smoothed particle hydrodynamics, involving marginally unstable disks of molecular H_2 (using up to $\sim 1 \times 10^6$ particles) generated masses of clumps, which, shortly after all of them are in place (after ~ 350 years) ranged in size from 1−5 Jupiter masses.[67] From these results the inner (solid) and outer giant gas planets (Jupiter and Saturn) would appear to share, in common, a rapidity-of-origin on a cosmic time scale.

The rich interstellar mix of organic physics/chemistry, noted earlier, appears to have carried over to our own Solar System. The relatively high abundance of C$^+$ and C^{2+} in the plasma of the recently discovered Kudo−Fujikawa comet is attributed to the evaporation and subsequent photoionization of atomic carbon from organic refractory compounds found in the cometary dust grains.[68] Data analyses from the dust-flux monitoring and comet-dust capture during the Stardust Discovery Mission spacecraft flyby of the comet 81P/Wild 2 have provided us with a treasure trove of new information on our planetary origins. These cometary particles (from 5−300 μm in size) are primarily silicate materials of solar system origin, formed close to the Sun, then transported far out to the Kuiper belt region before being incorporated into the comet.[69,70]

The close approach of the Cassini−Huygens spacecraft to Phoebe (Saturn's outermost moon) revealed the presence of Fe^{2+}-bearing minerals, bound water, CO_2, organics, nitriles, and CN compounds. Its density composition and orbital properties point to its origin as a captured body from the outer Solar System.[71] Refined simulations reinforce the argument that impact generation of satellites is a common outcome of late stage accretion of Pluto-Charon (Pluto's moon) as well as Earth-Moon.[72]

Spectral radar reflectance measurements, penetrating the thick N_2- and CH_4- rich atmosphere of the saturnian satellite, Titan, point to the possible existence of discrete "lakes" or a sea of liquid hydrocarbons beneath the photochemical haze in this atmosphere[73] in addition to an extensively exposed bedrock of water ice.[74] More recent near-infrared specular reflection studies argue to flat solid surfaces, presently devoid of liquid.[75] The observation of H_2O_2 in the Mars atmosphere, arising from the photodecomposition of water vapor, constitutes the first measurement of a key catalytic species in a planetary atmosphere other than our own.[76]

2.3. The Late Hadean to the Archaean

While it is reasonable to suspect that life may have developed on and in more than one occasion and place during these violent events, it would not likely have taken permanent hold before the end of the most intense phase of the bombardment and the appearance of a stable platform (landmass) and oceans, associated with the late Hadean.[77] Evidence for the contribution of plate-tectonics to landmass (continent) formation appears in a 20 km-long stretch of exposed rock (located near the North China village of Dongwanzi) believed to be a scrap of the oldest (2.7×10^9 year-old) known ocean crust which bears all the signs of generation at a midocean ridge some 200 million years into the (late) Archean.[78] Quartz globules and quartz veins from the Isua Greenstone Belt (IGB) of West Greenland preserve a record of an early Archean sea-floor, methane-brine, hydrothermal system operative at ~ 3.75 Gya, notable in that the salinity of early Archean seawater was not drastically different from today.[79] The question how can the first 20% of Earth history be understood, given the relative rarity (or outright absence) of a preserved rock record, has been addressed.[80] Along these lines, a newly developed thermometer, based on Ti incorporation into crystallizing zircon, argues to a more benign Hadean Aeon ($\sim 4.5−4.0$ Gya), possibly even characterized by oceans and continental crust like those of the present day.[81] But the debate continues, pending the collection of more supporting evidence.

A minimal environment that might have existed across the interface of these Aeons hints at a low ambient oxygen level ($\sim 1−2\%$ of the present atmospheric level) but sufficient to support aerobic recycling of the net organic carbon productivity in surface waters.[82] In addition, high-temperature hydrothermal emanations[83] gave rise to copious amounts of H_2S, H_2, Fe^{2+}, and CH_4 (Figure 3).
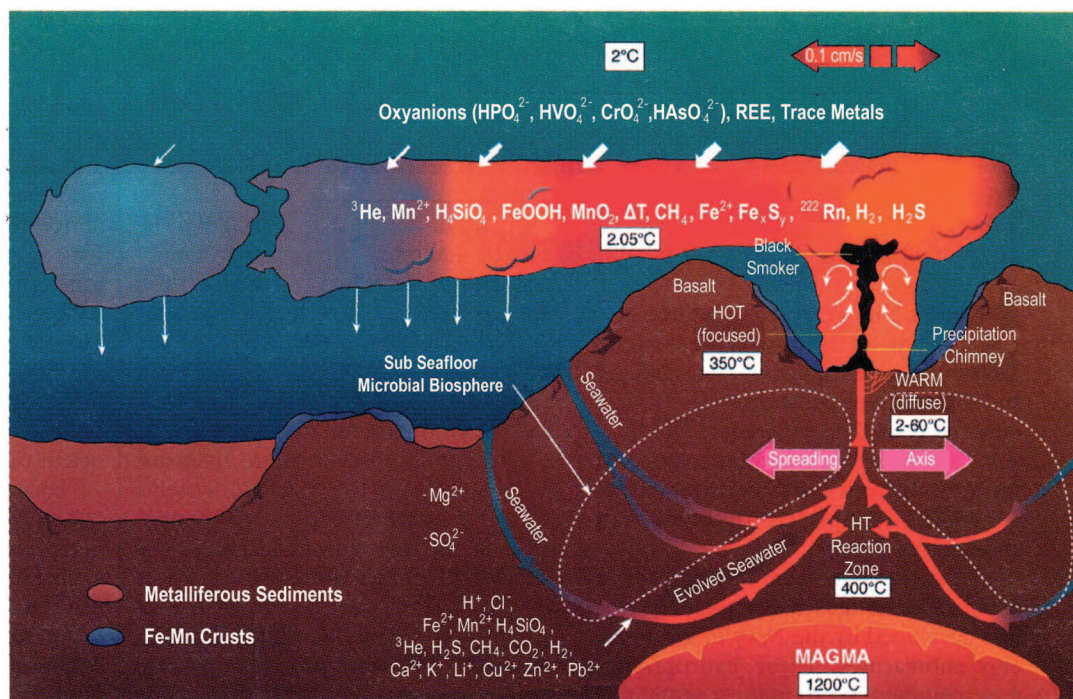
Figure 3. When intruding magma cracks crustal rock beneath the ocean, seawater rushes in to react with the rock, becomes heated, and rises to the seafloor, where it escapes from hydrothermal vents to form plumes known as black smokers. Within the plumes, which sometimes travel thousands of miles from the vent, further chemical reactions produce metal-rich particulates that settle on the ocean floor. (REE = rare-earth elements). Diagram by Gary Massoth/PMEL. Adapted with permission from ref 83. NOAA/Pacific Marine Environmental Laboratory.

Methane levels in the atmosphere may have been $\sim 10^3$ times higher than they are today. Since CH_4 is 25-fold more potent a greenhouse gas than CO_2,[84] this condition could have overwhelmed the major nonbiological source of free O_2 (the photodissociation of H_2O vapor).[85] Given the soft γ-ray emission that pervades the Milky Way Galaxy, and in spite of the high radiation tolerance of some ancient organisms (e.g., *Deinococcus radiodurans*), it is unlikely that, in the absence of an extreme depth to the Earth's atmosphere, terrestrial forms of advanced life could have survived this onslaught of radiation.[86]

The scenario of an interconnected and tightly integrated global geochemical sulfur cycle extending from the atmosphere to the mantle on Archean Earth emerges from several recent studies. A report of mass-independently fractionated sulfur isotope compositions for populations of sulfide inclusions found in diamonds mined in Botswana points to the presence of only trace levels of O_2 in Earth's atmosphere prior to $\sim 2.4-2.1$ Gya.[87] This thesis derives from the fact that only one natural process is known to produce mass-independent sulfur isotope effects: atmospheric photochemical reactions in the absence of O_2 or O_3, which shield the atmosphere from the UV (190–220 nm) radiation required for the reactions. The anomalous $\Delta^{33}S$ signature of sulfide inclusions in diamonds, arising from the photodissociation of SO_2 from volcanogenic origin, was transferred from the atmosphere through sedimentary sulfide to the mantle by subduction, where it was subjected to the mass-dependent fractionation laws associated with mantle processing. Diamond formation in the mantle encapsulated the sulfides and preserved them until the point at which they were brought to the surface by explosive volcanism. The low Archean SO_4^{2-} concentrations of this period (<200 μM) were main-

tained by volcanic outgassing of SO_2 gas and severely suppressed SO_4^{2-} reduction rates, allowing for a carbon cycle dominated by methanogenesis.[88] Carbon (like water, noted below) may have been copiously available, since the total amount of carbon stored in the atmosphere and oceans is thought to be negligible compared with that stored in the deeper parts of the upper mantle, possibly as a carbonate phase. Large scale volcanic eruptions, tapping into such a source, might rapidly transfer large amounts of CO_2 to the atmosphere.[89] Given the abundance of massive siderite-rich ($FeCO_3$) beds in ancient sediments and subsurface environments (>1.8 Gya), it has been proposed that CO_2, not CH_4, was sufficient and available to preserve the greenhouse-gas effect (trapping heat near the planet's surface) to counterbalance the diminished capacity (70–90%) of the faint young Sun to sustain a liquid ocean (the faint-sun paradox).[90]

2.4. Water

Water, in amounts sufficient to sustain these earliest metabolic processes, may not have been a limiting factor on Earth or Mars.[91] On Earth it might have accumulated by "dry" accretion, i.e., delivery from exogenous sources such as comets and meteorites after Earth had formed,[92] or "wet" accretion, i.e., delivery with anhydrous and hydrous silicate phases interspersed among the material inflowing to the growing planet.[93] Or, it may have come from an entirely unexpected source. Using secondary ion mass spectrometry (SIMS) and infrared microspectroscopic analyses on minerals of the type believed to predominate in the lower mantle (i.e., Mg-perovskite with some magnesiowüstite and Ca-perovskite), a 0.2 wt % (wt %) of H_2O content in the synthesized preparations of these minerals has been found. When this

capacity is integrated over the mass of the lower mantle, the total mass of stored water may be some five times more than that of the oceans.[94] The discovery of copious amounts of water observed with the Submillimeter Wave Astronomy Satellite (SWAS), in the vicinity of the dying (exploding) star, IRC+10216, by vaporization from its nearby comets[95] tells us that H_2O is a common ingredient in a solar system other than our own.

2.5. The End of a Beginning

The intense bombardment appears to have diminished by the late-Hadean to early-Archaean Aeons. Nevertheless, the continuing frequency of terrestrial[96] and oceanic[97] volcanism, recurrent eruptions of H_2S gas off the coast of Namibia,[98] and the cumulative evidence that impacts, eruptions, and major mass extinctions continue into the Quaternary Era[99] remind us that the maturation of planet Earth continues as a work in progress. In fact, noble gases, trapped since accretion, are still degassing from the mantle into the atmosphere.[100] Earth, it is suggested, presently accretes dust particles to the extent of some 30,000 tons per year, much of it from shocked (at pressures > 25 Gpa) hydrated, porous asteroids.[101]

3. Some Prebiotic Syntheses

3.1. In the Heavens

Given the truly diverse array of energy sources that could initiate carbon-chemistry synthesis, complex organic compounds should be expected in any sector of interstellar space or the Solar System that is rich in volatile elements. Indeed, a kinetic model has been projected for hydrocarbon formation in the solar nebula, by Fischer−Tropsch Fe/Ni catalysis, starting with H_2 and CO.[102] Isotopic evidence (especially enrichments in ^{15}N and ^2H) supports the idea that at least half of the insoluble organic matter in carbonaceous meteorites originated from sources that existed before the Solar System was formed. In contrast, soluble organic compounds in these meteorites, including amino acids, are generally thought to have been produced soon after the formation of the Solar System by the action of aqueous fluids on the asteroids that gave rise to the meteorites.[103]

Case in point: A gas (ice) mixture composed of H_2O/ CH_3OH/NH_3/CO/CO_2 of molar composition = 2:1:1:1:1, as representative of the interstellar medium, was deposited on an Al block at 12 K and irradiated by UV. The major components of this residue were saturated organic compounds containing carboxylic acids and hexamethylenetetraamine (HMTA). GC-MS analysis revealed the presence of 16 amino acids in the residue, 6 of which are protein constituents.[104] HMTA, a condensation product of NH_3 and HCHO, is a heterocyclic analog of adamantine ($C_{10}H_{16}$), with four nitrogens replacing the C−H groups at the bridgehead positions.[105]

Bias is evident with the discovery of an excess of L-amino acids in the Murchison meteorite. This enantiomeric excess in organic molecules in the protosolar system might have been generated by circular polarization as a result of scattering of UV light from a nearby star.[106] Alternatively, this property of handedness or chirality suggests prebiotic synthesis, which may be governed by certain geometric constraints, would more likely be carried out on a surface than in a dilute aqueous solution. Some L-amino acids are

known to adhere selectively to one of calcite's crystal faces, and the D-form to another.[107]

Using sonic spray ionization (SSI), follow-up studies on the innate capacity of serine (the putative product of the reaction between the interstellar molecules glycine and formaldehyde) to form homochiral octamers demonstrate that under mild conditions a solution containing L-serine and DL-glyceraldehyde exhibits only one prominent product $[Ser_6Glyc_6Na]^+$ (m/z = 1193), which fragments by loss of $C_6H_{12}O_6$ units, suggesting glyceraldehyde is present in the form of a dimer (hexose or an isomer) in the cluster.[108]

The presence of a variety of polyols in and indigenous to the (carbonaceous chondrite) Murchison and Murray meteorites in amounts comparable to amino acids[109] is further indication that molecular constituents commonly associated with a metabolic function are not uncommon in space. A variety of diamino acids, identified by using enantioselective GC-MS, were found in the Murchison meteorite, including L-2,4-diaminobutanoic acid and D- and L-2,3-diaminopropanoic acid, among others.[110] Similarities in the backbone structures of RNA and some diaminopeptide nucleic acids lend credence to the argument that peptide nucleic acids (PNAs) may have qualified as predecessor candidates to RNA in a pre-RNA world.[111]

Given the evidence that dense molecular clouds, being thousands of light years across, are vast, ubiquitous, chemical reactors, it has been proposed that interstellar ice photochemistry potentially offers a single simple explanation for the presence, deuterium-enrichment, enantiomeric excess of at least some amino acids and related compounds, and the energetics of N_2 fixation[112] rather than formation in liquid water on an early Solar System body. The use of low temperature photolysis on an astrophysically relevant ice mixture (H_2O/CH_3OH/NH_3/CO = 100:50:1:1) generated a very complex mixture of compounds, including amphiphiles and fluorescent molecules. Encapsulation and release of a polar dye from the amphiphilic components may indicate an ability of these entities to self-assemble into vesicular structures.[113]

3.2. ... and on the Earth

Like the environment in which it was generated and reared, primitive Earth, cobbled together from debris of the Solar System, was also a very likely and prolific laboratory for prebiotic syntheses. Thus, abiogenic CH_4 was shown to form rapidly from dissolved HCO_3^- in the presence of even small amounts of hydrothermally generated Ni−Fe alloys under reducing conditions.[114] Recent studies[115] demonstrate that Cr_2O_3, in combination with Fe-bearing oxides, is an effective catalyst for Fischer−Tropsch type synthesis of C_1, C_2, and C_3 hydrocarbons in the type of H_2-rich aqueous systems likely to be found in hydrothermal vents and aging ocean-floor deposits.[116]

While the predominant source of global hydrocarbons may arise from thermo- or bacteriogenic action, evidence based on $\delta^{13}C$ and δ^2H isotope signatures of CH_4 gas discharged from fractures and bore holes in the Canadian shield Kidd Creek mine also points to an abiogenic origin for this gas, probably by CO_2 reduction. The carbon isotopic depletion pattern was similar to that observed for the Murchison meteorite n-alkanes.[117] Application of pressures to 50 kbar and temperatures to 1,500 °C upon solid $CaCO_3$ and FeO wet with triply distilled water, all in the absence of any hydrocarbon or biotic molecules, produces a suite of

petroleum fluids: methane → hexane, branched isomers of these compounds, and several of the lightest of the *n*-alkene series.[118] Fabrication of complex molecular structures appears to have posed no barrier to abiotic synthesis. Several previously unknown higher diamondoids (a class of hydrocarbons with a carbon framework superimposable on the diamond lattice) containing 4 to 11 diamond-crystal cages have been isolated and crystallized from crude oil. Adamantane (noted above), the smallest diamondoid, is the single cage-shaped "parent" subunit of these nanometer-sized diamond molecules.[119]

Although Earth's primitive atmospheric composition of ~3.8 Gya remains uncertain, the most reducing atmosphere possible would have been composed of CH_4, NH_3, H_2, and H_2O. A dominant view in recent years has been that the atmosphere at life's origin(s) was composed of CO_2, N_2, and H_2O, with lesser amounts of CO, CH_4, and H_2. As a putative representation of these conditions, an equimolar gas mixture of CO, N_2, and liquid H_2O (5 mL) in a glass tube (400 mL) was subjected for 3 h at 279 K to a flux of high-energy (2.5−3.0 MeV) protons (a major component of cosmic rays). This energy is much greater than the bond dissociation energy of CO (11 eV) and N_2 (9.8 eV). In-situ generation of CO_2 occurs under these conditions. Subsequent workup of the reaction mixture revealed the presence of uracil, 5-hydroxyuracil, orotic acid, 4,5-dihydroxypyrimidine, nicotinic acid (niacin), and lesser amounts of adenine and guanine.[120] Since the reaction mechanisms for the synthesis of these compounds are uncertain, it is of no small significance that niacin and orotic acid are, respectively, key precursor molecules in the biosynthesis of the pyridine-nucleotide redox cofactors (NAD(H), NADP(H)) and the pyrimidine-mononucleotide constituents (UMP, CMP) of RNA.

Noteworthy also are the results of those who followed-up on the seminal work of Miller[121] subjecting what were thought to be the major components of Earth's atmospheric environment (CH_4, NH_3, H_2O, and H_2) to a variety of experimental conditions in the absence of O_2. Their investigations yielded a diversity of organic compounds. These included carboxylic and amino acids, sugars, aldehydes, porphyrins, and purines. COS (carbonyl sulfide, S=C=O), a simple volcanic gas, brings about the formation of peptides from amino acids under mild conditions in aqueous solution and may also have functioned as a condensing agent in phosphate chemistry.[122]

A reducing atmosphere may not have been essential for abiotic synthesis. Using a simulated prebiotic atmosphere of CO_2, N_2, and water vapor above liquid H_2O at 80 °C, pulsed with 60 kV, 30 mA at 20/s discharges, and W/Cu (cathode/anode) electrodes, one group[123] was able to demonstrate the presence of glycine, alanine, and NH_3, plus several unidentified peaks in the subsequent chromatographic analyses. Evidence of CuO on the copper electrode surface demonstrates the formation of oxygen during the reaction.

An abiotic "one-pot" synthesis of adenine, guanine, and diaminopurine was achieved by polymerization of concentrated (10 M) NH_4CN held at 80 °C for 24 h.[124] Samples of 0.1 M NH_4CN, held at −20 °C for 25 years and 2 months, respectively, were also found to contain adenine and guanine. The resulting yield pattern suggested that guanine synthesis, relative to adenine, is favored at lower temperatures. Since high concentrations of NH_4CN are obtainable only by freezing, it was thought this prebiotic synthesis might occur

in frozen regions of primitive Earth, Europa and other icy satellites, and the parent body of the Murchinson meteorite.

Using neat formamide ($HCONH_2$) at 160 °C for 48 h in the presence of selected inorganic catalysts ($CaCO_3$, kaolin, zeolite, alumina, silica, and kaolin), purine, adenine, cytosine, and 4(3H)-pyrimidinone were identified as the main reaction products of formamide condensation.[125] A wide range of selectivity and yield could be obtained depending on the catalyst used. The presence of inorganic components with layer or porous cavity structure could provide for a favorable local microenvironment relative to the problem of purine and pyrimidine fragility at high temperatures. In an extension of this work, a one-pot TiO_2-catalyzed synthesis, starting with neat formamide, has been used to generate thymine and 5-hydroxymethyluracil (not previously reported from a C-1 fragment), among other nucleobases.[126] These studies reinforce the argument that a facile route to the prebiotic synthesis of complex biogenic structures is very plausible.

Molecular structures of higher complexity than adenine and guanine may not have posed an impediment to prebiotic synthesis. From one perspective, all truly fundamental biomolecules—proteins, nucleic acids, sugars, cofactors, and so on—are intrinsically simple from a generational point of view.[127] Flavins, a group of redox catalyst cofactors, are indispensable in all cellular organisms. Riboflavin can be obtained in a 55% yield by heating a solution of 6,7-dimethyl-8-ribityllumazine in phosphate buffer at pH 7.3 under N_2 for 15 h in the absence of enzyme or any external source of carbon.[128] Lumazine (6,7-dimethyl-8-ribityllumazine), the biosynthetic precursor of riboflavin, can be formed from 5-amino-6-ribitylamino-2,4(1H,3H)-pyrimidinedione and 3,4-dihydroxy-2-butanone 4-phosphate in a dilute, neutral aqueous solution at room temperature without enzyme catalysis, albeit with a low regioselectivity. These observations support the hypothesis that flavin type molecules could have been formed naturally in prebiotic environments without enzyme catalysis.[129]

At a higher level of multimolecular assembly, abiotic membrane formation is well within the realm of probability. Using a pellet of $CaCl_2$ with $CuCl_2$, submerged in a solution of Na_2CO_3 (1.5 M) containing H_2O_2, NaI, and starch, the spontaneous formation of a cellular structure surrounded by a semipermeable membrane with the probable composition $Ca_x(CO_3)_y(OH)_z(H_2O)_v$ was demonstrated.[130] This system was able to sustain itself far from thermodynamic equilibrium. Structural details remain to be established.

3.3. The FeS Connection

Iron and sulfur, in various combinations, are found across stellar and planetary space. Thus, a broad infrared spectral band centered at ~23.5 μm, characteristic of FeS grains in primitive meteorites and pyrrhotite ([Fe, Ni]$_{1-x}$S) grains in interplanetary dust, is also seen in the infrared spectra of young stellar objects. This implies that FeS grains are an important but previously unrecognized component of circumstellar dust[131] with Fe_3O_4, amorphous carbon, and silicate grains identified in supernova ejecta from a high-red-shift quasar.[132]

On earth, the fertile environment of underwater hydrothermal vents (HTVs) spawns a brew of metal-rich particulates, including a variety of Fe_xS_y compounds[133] (Figure 4). Given the unique properties and chemical versatility of Fe and S and the entropic barrier to organic reactants coming together in a dilute oceanic medium, the presence of pyrite

Rich redox chemistry occurs beneath the ocean's floor
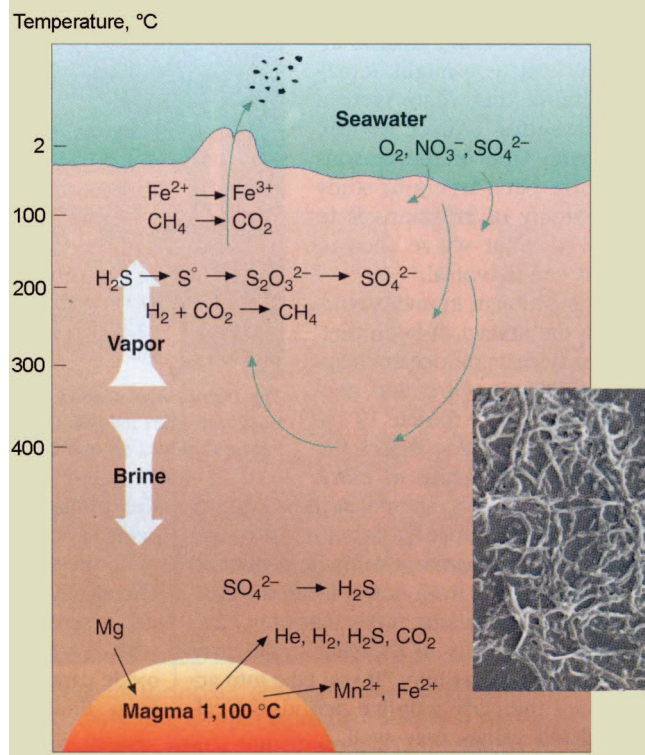
Figure 4. Intruding magma delivers reduced volatile compounds, metals, and heat into water-rich rock beneath the seafloor. Phase separation partitions volatiles and some metals into the vapor phase, and brines accumulate around the heat source to be released later in the vent fluids. This thermal and redox gradient provides a zone for chemical and microbial oxidation of reduced gases and metals as seawater circulates in the system. Microbial methane production and sulfur reduction are known to occur at temperatures as high as 110 °C. Filamentous sulfur (inset) recovered from particulates carried in the vent fluid is among evidence that microbially directed chemistry is occurring. Adapted with permission from ref 83. Copyright 1998 NOAA/Pacific Marine Environmental Laboratory.

(FeS_2) at these vents may have provided a habitat for both abiotic and biotic reactions.[134] From a H_2-rich-early-Earth-atmosphere viewpoint, the efficient production of organics would have led to an organic soup in the oceans and ponds on the early Earth.[135]

The strategy of using experimental conditions which mimic the high pressures and temperatures of these ancient (anoxic) vents to generate key metabolic building blocks has proven to be a fruitful approach. Thus, an aqueous slurry of coprecipitated FeS and NiS transformed CO and CH_3SH into the thioester, $CH_3–CO–SCH_3$, with subsequent hydrolysis to acetic acid. This reaction,

$$CH_3SH + CO + H_2O \rightarrow CH_3COOH + H_2S \quad (8)$$
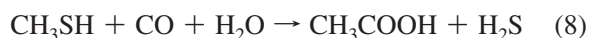
carried out at 100 °C in water at autogenic pressure and in a narrow pH range around 6.5, gave a yield up to ~40 mol %, based on CH_3SH.[136] Replacement of methyl mercaptan with benzyl- or phenylethyl-mercaptan gave rise to pheny-lacetic or phenylpropionic acids, respectively. When the amino acids L-phenylalanine (LF), L-tyrosine (LY), D-, L-tyrosine (DY, LY), and glycine (G) were individually incorporated into this reaction mixture at pH 7–10, dipeptide

bond formation was observed. Although peptide bond formation is endergonic, this reaction is facilitated within the ligand sphere of the sulfide mineral at a rate faster than hydrolysis.[137]

Similar vent-mimicking experiments were used to demonstrate the synthesis of pyruvic acid from an Fe-, S-, and CO-rich environment together with the presence of significant quantities of carbonylated iron–sulfur clusters (e.g., $Fe_2(RS)_2(CO)_6$). In a vent environment, where reduced hydrothermal fluids pass through sulfide-containing crust, significant concentrations of these potentially catalytic species will form. Advection of these high-pressure and -temperature products to the lower temperatures found near the crust–ocean interface may be more conducive to the survivability of important biomolecules such as α-keto acids.[138] With reductive amination of phenylpyruvate to phenylalanine using FeS and aqueous NH_4CO_3 (100 °C, pH 8.5)

$$RCOCOOH + 2FeS + NH_3 + 2H^+ \rightarrow$$
$$RCHNH_2COOH + FeS_2 + Fe^{2+} + H_2O \quad (9)$$
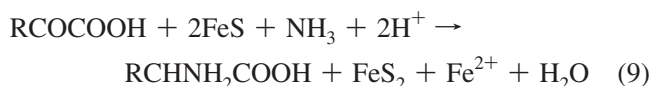
where CO_2 is catalytic, all of the individual reaction steps for a (anabolic) conversion of CO to peptides have now been demonstrated.[139] Subsequent findings have established the catabolic component of a peptide cycle, both segments of which are directly coupled with a net conversion of CO to CO_2.[140] Complex lipids of biotic origin (e.g., cholesterol, carotene, etc.) are thought to be recycled in anoxic sediments by stereoselective reduction to their corresponding "-ane" counterparts (i.e., cholestane, carotane) using H_2S arising from the microbial oxidation of organic matter at the expense of sulfate. The cumulative effects of these biotic and abiotic hydrogenation reactions generate long-lived hydrocarbon biomarkers, evident in the abundant organic carbon debris found in sediments and rocks of Earth's oceanic crust, and they constitute a major preservation pathway of sedimentary organic carbon.[141]

Abiotic ammonia might have been more readily available on early Earth than previously realized. For example, the ability to generate NH_3 from NO_2^- and NO_3^- and N_2, rapidly and in significant yields by mineral-catalyzed reduction under a variety of experimental conditions (~300–700 °C; 0.1–0.4 GPa) which mimic crustal and oceanic hydrothermal conditions could have provided a significant source of NH_3 to the Hadean ocean.[142] Or, it may have also been significantly augmented by the prebiotic synthesis of NH_3 from N_2 using H_2S as reductant and freshly precipitated iron sulfide as a mediator. Trading on the favorable free energy change ($\Delta G°$ = −38.6 kJ/mol) for the reaction

$$FeS_{(s)} + H_2S_{(aq)} \rightarrow FeS_{2(s)} + H_{2(g)} \quad (10)$$

it has been demonstrated[143] that this redox system is able to reduce dissolved molecular nitrogen to NH_3 at ~80 °C and atmospheric nitrogen pressure

$$N_{2(g)} + 3FeS + 3H_2S_{(aq)} \rightarrow 3FeS_{2(s)} + 2NH_{3(g)} \quad (11)$$
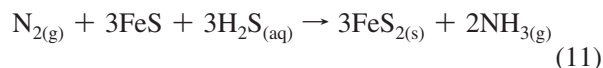
with a yield of ~3 mmol of NH_3/3 mol of FeS. The special surface features of freshly precipitated iron sulfide, providing a "library of different Fe–S clusters", may be instrumental in lowering the high activation energy associated with molecular nitrogen. Juxtaposing the very complex active site

of the archaeal/bacterial nitrogenase-driven transformation (see below) to this putative prebiotic iron sulfide-driven reaction serves to remind us how very little we know of the driving forces and tremendous amount of intervening physics, chemistry, and biology involved in these transitions.[144]

What is strikingly evident across the prebiotic world, interstellar or terrestrial, is the innate capacity of matter/energy to carry out covalent bond syntheses (the making of molecules), self-assembly (the ordered ensembles of molecules, usually involving noncovalent interactions), and self-organization.[145] Components of any size, from snow crystals to galaxies, can self-assemble in a permissive environment.[146] The innate capacity of short peptide motifs to self-assemble into amyloid-like fibril structures and/or nanotubular arrangements forming encapsulated structures may have served as highly ordered templates for nucleotide assembly.[147]

4. At the Interface: From Prebiotic to Biogenic

The antiquity of the genetic code is evident from its distribution. Archaea, Bacteria, and Eukarya use the same set of codon assignments, indicating the code predates their divergence[148] on the ring or tree of life.[149] By some 3.8−3.5 Gya, most of the principal biochemical pathways that sustain the modern biosphere had evolved, were global in scope,[150] and had achieved remarkable levels of metabolic sophistication[151] before the end of the Archaean Aeon ∼2.5 Gya.[152] Given this "sudden" proliferation, in what time frame during its gestation could Earth have provided a hospitable environment for biogenic life? When, where, and how did it arise? With their diverse elemental content and large mass of organic compounds, atmospheric aerosol particles, of the same size as single-celled organisms, are proposed as enticing candidates for prebiotic chemical reactors when functioning as inverted micelles.[153] The chemical properties of the various side chains of proteins, along with a selection of metal ions and cofactors that can be incorporated into the folded structures, not only permit folding but also define the fundamental chemistry of life.[154] Did the fact that cytosine (C) and uracil (U) could have arisen from the sequential hydrolysis of 2,4-diaminopyrimidine (D) have played a role in the molecular evolution of the genetic alphabet?[155]

4.1. Self-assembly

Self-assembly processes[156] are notably evident and were pervasive even among these earliest of life-forms. The complexity of membrane lipid structures found in Archaean thermoacidophiles[157] could have mirrored a lipid world prior to the emergence of life, given that lipid vesicles can self-assemble without the need for enzymes.[158] Additional interface hallmarks include but are not limited to: Action on a surface as opposed to solution chemistry; biomineralization;[159] formation of biofilms and microbial mats;[160] quorum-sensing;[161] and horizontal gene transfer, HGT.[162] In fact, a case has been made that HGT, not vertical inheritance, was primary and pervasive in the primitive evolutionary dynamic at the progenotes (very simple cellular entities) stage.[163] However, the possibility that viruses can originate genes and then colonize prokaryotes (or eukaryotes) to give the appearance of lateral (horizontal) gene transfer cannot be discounted.[164] In addition, the stability of bacterial or biofilm communities is enhanced by their diversity,[165] providing an opportune environment for HGT.[166] For obvious reasons, caution must be exercised when assessing microbial phylogenetic relationships.[167]

4.2. Biomineralization

Of the several proposed suggestions to account for an innate capacity of some anaerobic microorganisms to respire on a solid surface such as α-Fe$_2$O$_3$ (hematite) or α-FeOOH (goethite), a dominant mechanism appears to involve the direct transfer of electrons from the cell surface to the mineral. A variety of biomolecules (including cytochromes, quinones, and dehydrogenases) have been identified as part of this electron transport pathway.[159b]

Atomic force microscopy (AFM) has been used to probe the interface between a living cell of the metal-reducing bacterium, *Shewanella oneidensis*, and the 010 surfaces of α-FeOOH and α-AlOOH.[168] α-AlOOH (diaspore) is isostructural with goethite and has similar surface properties at the nanoscale level in anaerobic and aerobic solutions. Energy values in attojoules (10^{-18} joules) derived from these measurements have shown that *S. oneidensis* responds to the surface of goethite by rapidly developing retraction energies at the interface 2 to 5 times stronger under anaerobic as opposed to aerobic conditions. These data indicate that, after the recognition of α-FeOOH as a terminal electron acceptor, *S. oneidensis* actively mobilizes, a protein (a 150-kD putative iron reductase) in the outer membrane that specifically interacts with the mineral surface, facilitating electron transfer.

In a variation on this theme, studies conducted on biominerals in an iron oxyhydroxide-encrusted biofilm collected from flooded underground tunnels reveal that microbially produced polysaccharides can template the nucleation of pseudosingle crystals of akaganeite (β-FeOOH) with aspect ratios of ∼10^3:1.[169] From these studies it is inferred that cells extrude polysaccharide strands to localize precipitation reactions. A subsequent proton-generating reaction sequence

$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2{}^+ + 2H^+;$$
$$Fe(OH)_2{}^+ \rightarrow FeOOH + H^+ \quad (12)$$
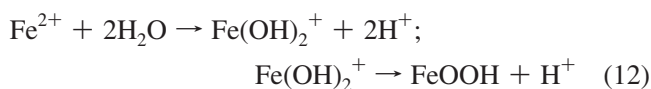
localized near the cell wall of these neutrophilic Fe-oxidizing bacteria, enhances the proton motive force, thereby increasing the energy-generating potential of the cell. In this vein, the pili of *G. sulfurreducens* (and other organisms) appear to serve as biological nanowires, transferring electrons to the Fe(III) oxides surface from the cell surface.[170]

Are these earliest life-forms of terrestrial (land-water interface) origin?[171] Or did they arise in the vicinity of midocean hydrothermal vents?[172] Was LUCA (the last universal common ancestor) a hyperthermophilic (or psychrophilic) organism, as were the ancestors of the Archaea and Bacteria Domains,[173] or has the LUCA concept evolved to encompass the last common community?[174] Could they have been deposited as a result of intensive meteorite or cometary body impacts with Earth during the first Aeon?[175] Perhaps they were of chemoautotrophic origin.[176] Or, does the metabolist theory[177] provide a more cogent kick-start explanation for life's earliest chemistry? Perhaps the theory of emergence of templated-information and functionality (ETIF) offers a more encompassing perspective.[178] Persuasive arguments can be marshaled to support these various positions.[179] However, when we step back and look at the

whole mosaic, many gaps, inconsistencies, and uncertainties still remain. Much more evidence is needed before we can begin to answer these questions with any degree of certitude.

4.3. A Few Tools of the Trade

The history of life on Earth is etched in the geological strata, the fossil record, and the genomes of contemporary organisms.[180] Sleuthing in this geological stone and rock record leans heavily on proven radioactive-isotope decay schemes. Fossil tracking exploits the fact that living organisms tend to preferentially take up the lighter isotope (e.g., ^{12}C vs ^{13}C) of various elements (e.g., C, S, O, Fe), leading to a bias against the heavier nuclide in biotic cell debris.[181] Given a lack or paucity of morphological and/or molecular fossil evidence from these Aeons, this investigative tool has found widespread use but still must be used with interpretive caution.

4.4. Playing the Dating Game

Evidence for the presence of microscopic sulfides in 3.47 Gya barite ($BaSO_4$) deposits from North Pole, Australia, based on $^{34}S/^{32}S$ isotope ratios (expressed as $\delta^{34}S$ %), is indicative of microbial sulfate reduction. This evidence of biogenic origin is based on observations that sulfides, generated by the oxidation of H_2 or organic matter with sulfate at concentrations > 1 mM, are highly depleted in ^{34}S by some 10−40% compared to the SO_4^{2-}, with fractionations decreasing to near 0% at lower concentrations. The organism responsible for these reactions is tentatively positioned immediately above the branch point of the hyperthermophilic *Thermodesulfobacterium* lineage in the Bacterial domain on the tree of life.[182] Apparently, the facile ability to metabolize sulfur compounds was widespread throughout the Domains, Bacteria, and Archaea.[183]

The discovery of pyritic filaments, the probable fossil remains of threadlike micro-organisms, in a 3.235 Gya deep-sea volcanogenic massive sulfide (VMS) deposit from the Pilbara Craton, in NW Australia, suggests a flourishing habitat of thermophilic microbiota in subsea-floor niches adjacent to discharging hydrothermal fluids. A biotic origin is inferred for these filaments from their sinuous morphology, length uniformity, and intertwined habit, which are compatible to those of Archaean and younger microfossils.[184] Evidence from the micrometer-scale mineralized pillow lavas of the Barberton Greenstone Belt in South Africa indicates that microbial life colonized these Mesoarchaean subaqueous volcanic rocks soon after their eruption some 3.5 Gya.[185]

Using a very sensitive ion-microprobe technique, the presence of ^{13}C-depleted (vis à vis ^{12}C) reduced carbon in graphite inclusions within grains of apatite (basic calcium phosphate) as indicative of a biogenic origin in banded iron formations (BIF) from the Isua supercrustal belt of Western Greenland has been reported.[186] These rocks, of sedimentary origin, are at least as old as their metamorphic age ($\sim$3.8 Gya). However, the age of these samples and the cited characteristics of the BIF are in dispute.[187]

Evidence for a terrestrial biomass of age $\sim$2.6−2.7 Gya has been found in ancient carbonaceous soils from the Mpumalanga Province of South Africa.[188] This assessment is based on a diversity of measurements, which include the crystallinity and H/C ratio of the organic matter, the positive correlations among the contents of bioessential elements, carbon, nitrogen, and phosphorus, and the isotopic composition of the host rocks.

4.5. But Doubts Arise

A diverse assemblage of filamentous microbial fossils of some $\sim$3.5 Gya, detected in the Early Archean Apex chert from northwestern Western Australia, is indicative of a biotic (biological) origin.[189] These results are not without controversy. It is argued that ancient filamentous structures should not be accepted as being of biotic origin until all possibilities of their abiotic (nonbiological) origin have been exhausted.[190] A reexamination the Apex chert material using laser-Raman imagery[191] reportedly confirms the earlier results of a biotic origin for these fossils. However, the demonstrated formation and growth of filamentous materials under alkaline, mildly hydrothermal conditions, whose morphologies and Raman spectra closely mimic those of the Western Australian microfossils, points to their abiotic origin.[192] In a similar vein, claims made for the biogenic origin of magnetite (Fe_3O_4) nanocrystals inside 3.9 Gya carbonate in a Martian meteorite are in dispute.[193] Given the fact that abiotic processes can fractionate the Fe isotopes to the same extent as biotic processes, it is noted that Fe isotopes on their own do not provide an effective biosignature.[194] The controversy continues.[195]

Enrichment in the heavy isotopes of Fe found in the >3.83 Gya quartz-pyroxene banded rocks of Akilia Island, Greenland, supports a sedimentary rather than an igneous origin for their formation.[196] In this connection, the upward diffusion of O_2, NO_3^-, and SO_4^{2-} from the deep basaltic basement of the sediment some 4400 m below the sea floor points to a heretofore unrealized wealth of unique microbial processes occurring in the deep, dark environs far below the sea floor.[197] Taken together, these studies would appear to lend credence to the thesis of a biotic origin from some of these rocks, but this has been challenged.[198]

4.6. A Molecular Fossil?

While isotopic and other geological evidence offer useful dating clues, the results may be equivocal. Biomarkers are potentially useful because each Domain, Archaea, Bacteria, and Eukarya, has signature membrane lipids with relatively stable complex carbon skeletons. Molecular fossils, recovered from $\sim$2.7 Gya Archaean kerogenous shales taken from depths of 700 m in the Pilbara Craton of Northwest Australia, were found to be rich sources of bacteriohopanepolyols (BHP). The abundant presence of 2α-methylhopanes, a signature membrane lipid of cyanobacteria, argues to the existence of eukaryotic life and oxygenic photosynthesis some 2.5−2.7 Gya.[199] Given the present conflict between fossil- and molecular-based evolutionary time scales,[200] interpretive caution is called for with these dates.

4.7. Microbial Speleogenesis

Microbial activity is increasingly implicated in geochemical processes across a broad range of aqueous systems. However, we are only just beginning to understand how microbes and geochemical systems interact. Microbial evolution is one of metabolic diversity rather than cell complexity and organism structure as found in higher plants and animals.[201] In contrast to the strategy of sulfate reducing bacteria (see below, section 6.6), cave building/enlarging

filamentous ϵ- and γ-proteobacteria, found in Lower Kane Cave, Wyoming, use a different approach, referred to as sulfuric acid speleogenesis (SAS). These organisms (sulfur-oxidizing bacterial commmunities) colonize the limestone cave walls, consuming H_2S within the subaqueous environment to generate H_2SO_4. Here the acid reacts with and replaces the carbonate host rock with gypsum

$$H_2SO_4 + CaCO_3 + H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2 \tag{13}$$
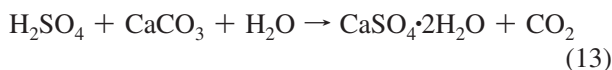
resulting in the removal of mass and an increase in void volume as $CaSO_4$ dissolves in the groundwater. The metabolic consequences of an active microbial ecosystem change the model for sulfuric acid speleogensis.[202]

5. A First Ecosystem?

Some of the earliest manipulative skills of Nature appear to have been directed to the practice of oxidation−reduction on C-1 compounds (e.g., CO, CO_2/HCO_3^-, CH_4, HCHO, CH_3OH, CH_3NH_2), with a supporting cast of H_2, H_2S, N_2, P, and SO_4^{2-}, using a dozen or so elements with atomic mass above 50 as structural elements in proteins or cofactors in enzymes.[203] This drama might have played out in a hydrothermal vent field with an Archaean organism able to grow at 121 °C (∼250 °F), using iron(III) as its (only known) electron acceptor.[204] Evidence suggests Fe−CO−CN−H species may qualify as minimalist biomimetic models of Fe-only and possibly the [Ni−Fe] hydrogenases.[205] A report on the synthesis of the first trinuclear [NiFe] cluster that shows the structural as well as functional properties of the active site of [NiFe] hydrogenases[206] reinforces this thesis.

5.1. Methanogens, H_2, and Hydrogenases to the Rescue

A subsurface environment and Archaean dominant microbial community lacking organic carbon, but with a source of geologically produced H_2, has been identified at Lidy Hot Springs in Idaho.[207] Similarly, an endolithic microbial H_2-driven community inhabits the Yellowstone Wyoming geothermal system.[208] Analyses of the 16S rDNA recovered from the deep circulating hydrothermal habitat in Idaho revealed that no fewer than 62 of the 65 archaeal sequences recovered appear to be from hydrogen-oxidizing CH_4-producing (methanogenic) microorganisms that catalyze the disproportionation reaction

$$4H_{2(g)} + CO_{2(aq)} \rightarrow CH_{4(g)} + 2H_2O_{(1)}$$
$$\Delta G° = -131 \text{ kJ mol}^{-1} \tag{14}$$
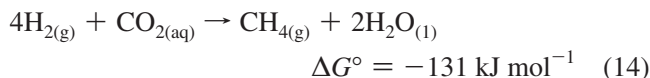
in an ecosystem where they form the base of the food chain. This reaction may be driven by a member of a novel class of metal-free hydrogenases[209] that catalyze the reversible hydrogenation of N^5,N^{10}-methenyl-5,6,7,8-tetrahydromethanopterin to yield N^5,N^{10}-methylene-5,6,7,8-tetrahydromethanopterin:

$$H_2 + CH \equiv H_4MPT^+ \leftrightarrow CH_2 = H_4MPT + H^+$$
$$\Delta G°' = -5.5 \text{kJ mol}^{-1} \tag{15}$$
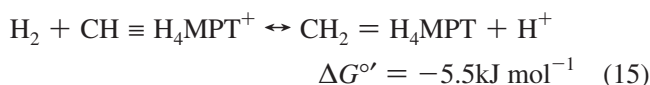
Unlike the Fe-only-, Ni−Fe-, and Ni−Fe−Se-hydrogenases,[210] which bind and activate H_2, this enzyme activates a hydrogen acceptor, which then directly reacts with H_2.[211] It may represent a more primitive form of this versatile group

of enzymes.[212] However, this third, "metal-free" class of hydrogenases was recently shown to contain an essential Fe atom.[213] In fact, the presence of an Fe center and carbonyl ligands are now recognized as a defining characteristic of hydrogenases.[214]

A methanogen, methylamine methyltransferase (MAMT), from the Archaeon, *Methanosarcina barkeri,* found in fresh water lake sediments, catalyzes the initial activation step in the sequence of reactions leading to the transformation: methylamine(s) $\rightarrow$ methane. This enzyme is distinguished by the presence of a new, genetically encoded amino acid, L-pyrrolysine (the 22nd amino acid), in an active site of the enzyme.[215] Like selenocysteine (Sec), the 21st amino acid, pyrrolysine is encoded by an RNA nucleotide triplet, UAG (vs UGA for Sec), both of which ordinarily serve as stop codons to halt translation of mRNA. The question as to how this atypical genetically encoded residue is inserted into proteins has been resolved.[216] Synthetic L-pyrrolysine (L-pLys) is attached as a free molecule to $tRNA_{CUA}$ by an archaeal class II aminoacyl-tRNA synthetase (PylS). This enzyme activates pyrrolysine with ATP and ligates pyrrolysine to $tRNA_{CUA}$ *in vitro* in reactions specific for pyrrolysine. The addition of pyrrolysine to *Escherichia coli* cells expressing the *pylT* (encoding $tRNA_{CUA}$) and *pylS* genes results in the translation of UAG *in vivo* as a sense codon. This discovery reaffirms the notion that, if something can be done by experiment, it has probably been done earlier by nature.[217]

A breakthrough in the study of Fe-only hydrogenases was made when X-ray crystal structures of *Clostridium pasteurianum*[218] and *Desulfovibrio desulfuricans*[219] were reported.[220] The active site of these enzymes consists of an $Fe(\mu$-$SR)_2(CN)_2(CO)_3 L_n$ core (L = H_2O/H_2) and a thiolate-linked $Fe_4S_4(SR)_4$ cluster, simple analogs of which can be effective catalysts for the reduction, $2H^+ + 2e^- \rightarrow H_2$.[221] Given the structural simplicity of the dithiolate cofactor ($-SCH_2NHCH_2S-$) at the active site of these enzymes, diiron carbonyl sulfide, when added to a premixed THF solution of paraformaldehyde and amine at 0 °C followed by warming to room temperature, condenses to yield the corresponding azadithiolates:[222]

$$Fe_2(SH)_2(CO)_6 + HCHO + RNH_2 \rightarrow$$
$$Fe_2[(SCH_2)_2NR](CO)_6 + 2H_2O \tag{16}$$
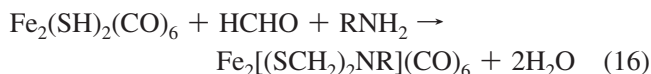
Thus, $Fe_2[(SCH_2)_2N\text{-}t\text{-}Bu](CO)_6$ and $Fe_2[(SCH_2)_2NCH_2Ph]$-$(CO)_6$ were obtained from *tert*-butylamine and benzylamine in 91 and 87% isolated yields, respectively. The relative manipulative ease with which these putative Fe-only hydrogenase active-site-core analogs can be assembled from simple materials is especially noteworthy, given the close end-product resemblances to the $Fe_2(RS)_2(CO)_6$ clusters derived from the vent-mimicking experiments noted earlier. It may be that the ultimate ancestor of the distinctly organometallic active-site of iron hydrogenases is diironhexacarbonyldisulfide, i.e., a fragment of the mineral ironsulfide, rendered molecular and mobilized by carbon monoxide.[223]

6. A Sampling of Metalloclusters

Nature's catalytic strategy−tapping into the redox properties of monocarbon molecules to extract energy for biomass production (noted above)−is not restricted to iron sulfide clusters. Other transition elements (e.g., Cu, Mo, Ni, V, W, Zn, etc.) incorporated into metalloclusters[224] may be a

hallmark feature of the very early stages in biochemical evolution,[225] allowing for reaction diversity as a function of metallocluster/cofactor modification.

Consortia of highly conserved proteins are required for the biosynthesis, intracellular metal trafficking, and maturation of [Fe–S] clusters[226] and their insertion into various protein partners, the basic features of which have been strongly conserved throughout most of Nature.[227] Some of these Fe–S-proteins (e.g., ferredoxins (Fd), rubredoxins (Rd)) show electron transfer activity; others function in enzymatic catalysis.[228]

A defining feature of the mononuclear molybdenum enzymes (and a variety of tungsten-containing enzymes as well) is the presence of a pterin cofactor with the Mo coordinated, not directly, but to the pterin moeity via its dithiolenes side chain.[229] Incorporation of the dithiolene moiety into a precursor molecule to form molybdopterin (MPT) is catalyzed by MPT synthase in a highly conserved biosynthetic pathway beginning with a guanosine derivative found in virtually all organisms from archaea to humans.[230] The final step in the molybdenum cofactor (Moco) biosynthesis pathway is associated with at least two unexpected processes: (i) The adenylation of MPT and (ii) Cu-dithiolate complex formation prior to the cleavage of the Cu-MPT-AMP complex to activate and transfer the Mo atom to MPT.[231] Taken collectively, these characteristics are indicative of the antiquity, stability, and central role of the metallocluster strategy as it played out early in Nature's seemingly primitive organisms. This pervasive flexibility is evident in the several examples cited below.

6.1. Hydrogenase

The hyperthermophilic Archaeon and anaerobic heterotroph *Pyrococcus furiosis* (*Pf*) grows at ∼100 °C and is known to utilize several types of hydrogenase enzymes, giving it multiple sources of reducing equivalents (e.g., H_2, ferredoxin (Fd), NADPH) and a metabolic and motile versatility,[232] including the ability to generate H_2 from glucose-6-phosphate (G6P) via the oxidative pentose phosphate pathway at a ∼97% yield.[233] The Fd of *Pf*, which displays monomer/dimer equilibrium as a function of ionic strength, is stable in denaturing gel equilibrium, even following sterilization at 121 °C.[234] The ability of *Pf* to thrive in a hyperthermophilic environment has been traced to the high degree of compactness and hydrophobic character of its proteins relative to its mesophilic (bacterial) counterparts. These organisms (e.g., *Thermotoga maritima*) followed a different evolutionary strategy in readapting their protein structure to a thermophilic environment.[235]

Pyrobaculum islandicum, a hyperthermophilic Archaeon, grown on H_2, CO_2, and acetate, uses the citric acid cycle in both oxidative and reductive directions for heterotrophic and autotrophic growth, respectively. Here it is suggested that acetylated citrate lyase and AMP-forming acetate/CoA ligase, but not ATP citrate synthase, work opposite citrate synthase to control the direction of carbon flow in this cycle,[236] illustrating once again the nuanced metabolic capabilities of these ancient organisms.

The strategy utilized by many H_2-consuming *Desulfovibrio* (sulfate reducing bacteria, SRB) species appears to involve an [Fe]-hydrogenase enzyme and a low redox potential cytochrome (c_3) protein acting in tandem to split or synthesize H_2, and facilitate protein and electron transport, respectively. The enzyme component is made up of two subunits

of 10 and 42 kDa. The larger subunit contains a ferredoxin-like domain with 2[4Fe-4S] clusters and a so-called H cluster constituted of a regular [4Fe-4S] cluster bridged to an active site Fe binuclear center.[237] While the complex molecular structures of intermediary metabolism were fully functional in these extremophiles, the origins of their complement of precursor molecules continue to elude us.

6.2. FMFDH/AOR

In strictly anaerobic organisms, an enzyme involved in the reduction of CO_2 to CH_4, formylmethanofuran dehydrogenase (FMFDH), is a molybdenum or tungsten iron–sulfur protein.[238] The aldehyde ferredoxin oxidoreductase (AOR) enzymes, found in hyperthermophilic archaea and in acetogenic and sulfate-reducing bacteria, are "true" tungstoenzymes in that they are phylogenetically distinct from the major classes of molybdoenzymes, with AOR of *Pyrococcus furiosis* (*Pf*) the first to be characterized at atomic (2.3-Å) resolution.[239]

6.3. CODH

The Ni-containing carbon monoxide dehydrogenase (CODH) family can be divided into four classes I–IV,[240] depending on enzyme functionality, and may contain Ni, Fe, S, and/or Co in a subunit or cluster. *Rhodospirillum rubrum* (CODH$_{Rr}$), a class IV CODH, grows on CO as its energy source using a NiFeS CODH to catalyze the reaction[241]

$$CO + H_2O \leftrightarrow CO_2 + 2e^- + 2H^+ \qquad (17)$$
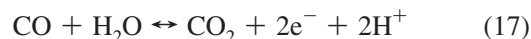
CODH variants with substitutions at several conserved cysteine (C) and histidine (H) residues were produced by site-directed mutagenesis of the encoding *cooS* gene.[242] Replacement of C_{531} with alanine (A) generated a variant, C531A CODH, with significant H_2 uptake hydrogenase activity ($H_2 \rightarrow 2H^+ + 2e^-$). Pretreatment for 30 min with CO enhanced this activity some ∼2.5 times. Replacement of His$_{265}$ with valine (V) generated a variant (H265V CODH) with an induced hydroxylamine reductase activity

$$NH_2OH + H_2 \rightarrow NH_3 + H_2O \qquad (18)$$

When Fe replaced Ni in the active site, the resulting mutant also displayed considerable NH_2OH reductase activity.

6.4. CODH/ACS and ACDS

Crystal structure analysis at 2.2 Å resolution of a bifunctional carbon monoxide dehydrogenase/acetyl coenzyme A synthase (CODH/ACS or ACS/CODH) from the acetogenic bacteria, *Moorella thermoacetica*, used to convert CO_2 to acetyl-Co-A, showed it to contain a [Fe$_4$S$_4$] cubane bridged to a Cu–Ni-binuclear site in the A-cluster of the ACS subunit. No metalloprotein active site with three different transition metal ions has been previously reported, suggesting a newly discovered role for Cu in biological systems.[243] While the mechanistic details of these reactions remain to be clarified, given the role of CH$_3$–Co(III)–CFeSP (a cobalt/corrinoid–Fe–S protein) affiliated with the A-cluster in the final step of CH$_3$(CO)SCoA formation, it would appear that the overall conversion of CO_2 to acetyl CoA involves the participation of four transition metals: Co, Fe, Ni, and Cu. However, the presence of Cu as the bridging metal in the

ACS active site has been challenged.[244] A 1.9 Å crystal structure resolution points to a closed form containing 1 Ni and 1 Zn at its active-site metal cluster, whereas the open (catalytically active) form has 2 Ni ions at the corresponding positions:[245] Cu or Ni? The debate on CODH/ACS continues.[246] Multimolecular structures, assembled to catalyze linked metabolic functions, are evident in the most primitive organisms. Methanogenic Archaea can synthesize acetyl units when grown on C-1 substrates or execute acetyl C−C bond cleavage when grown on acetate. Acetyl-CoA decarbonylase/synthase (ACDS), the multienzyme complex responsible for this overall reaction,

$$AcetylCo\text{-}A + H_4SPt + H_2O \leftrightarrow CoASH +$$
$$CH_3\text{-}H_4SPt + CO_2 + 2H^+ + 2e^- \quad (19)$$
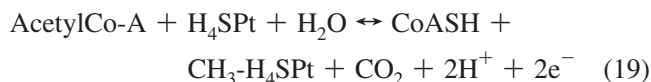
(where tetrahydrosarcinapterin, H_4SPt, serves as the methyl group acceptor) contains five different polypeptide subunits (α, β, γ, δ, ε). The β subunit (CdhC) contains the active site for acetyl-enzyme formation. Both the native β and α (CdhA, CODH) subunits contain Fe in the form of Fe/S clusters, in addition to Ni.[247] When two forms of the *Mathanosarcina thermophila* β subunit were overexpressed by this group in anaerobically grown *E. coli* using recombinant techniques, both—the full-length 472-amino acid ACDS β subunit (CdhC) and the truncated version (CdhC*) lacking 75 amino acids at the C terminus—were found to contain similar Fe/S cluster contents, but they lacked nickel and were inactive in catalysis of acetyl group transfer at low redox potential. Incubation of the overexpressed CdhC and CdhC* with $NiCl_2$ generated high activity to the extent that the kinetics of Ni incorporation was correlated with the time course for enzyme activation. The data presented are consistent with a structure for the Ni−Fe/S center similar to that of the clostridial CODH/ACS (noted above) but containing a binuclear metal site with nickel residing at both positions in an $Ni_2[Fe_4S_4]$ arrangement.

6.5. Some N_2−Cycle Enzymes

6.5.1. Nitrogenase

When Mo is incorporated into the mix of FeS-cluster chemistry, we come up against one of Nature's most complex and fascinating catalysts.[248] Nitrogenase, the global gatekeeper of the transformation[249]

$$N_2 + 8e^- + 16MgATP + 8H^+ \rightarrow 2NH_3 + H_2 +$$
$$16MgADP + 16P_i \quad (20)$$
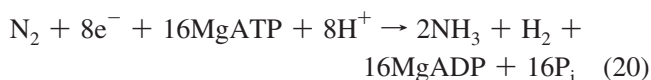
whose origins may predate the rise of O_2[250], occurs in a variety of genetically distinct forms. These include the molybdenum-containing (*nif*), vanadium-dependent (*vnf*), iron-only (*anf*), and *nif/vnf/anf*-independent variants. The classical nitrogenase (*nif*) enzyme catalyzing this reaction is composed of two proteins: The dinitrogenase component (MoFe protein, an $\alpha_2\beta_2$ heterotetramer, M_r ~240 kDa), and the dinitrogenase reductase component (Fe protein, a homodimer, M_r ~64 kDa). The MoFe protein contains two sets of two unique metal−sulfur clusters: an Fe_8S_7 or P-cluster and an FeMoco (iron−molybdenum cofactor) cluster containing Mo/Fe/S/-homocitrate in a 1/7/9/1 ratio. The homodimer (Fe protein) contains two nucleotide (MgATP/MgADP) binding sites and one conventional Fe_4S_4 cluster, bridging the two subunits.[251]

In the absence of substrates, the FeMo-, FeV-, and FeFe-nitrogenase variants reduce protons to H_2, but in the presence of N_2, the electron flux is divided between reduction of N_2 to form NH_3 and protons to form H_2.[252] Based on studies of the limiting stoichiometries of these three (M = metal) types of nitrogenase,

$$M = Mo: \quad N_2 + 8H^+ + 8e^- \rightarrow 2NH_3 + 1H_2 \quad (21)$$

$$M = V: \quad N_2 + 12H^+ + 12e^- \rightarrow 2NH_3 + 3H_2 \quad (22)$$

$$M = Fe: \quad N_2 + 21H^+ + 21e^- \rightarrow 2NH_3 + 7.5H_2 \quad (23)$$
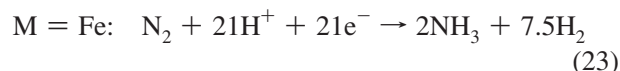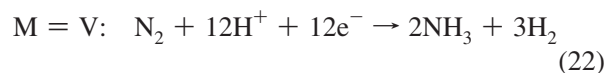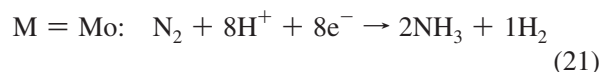
by this group, it is postulated that, irrespective of where N_2 binds to the cofactor, the Mo atoms affect the reactivity of the cofactor in a way that facilitates efficient N_2 fixation. The Mo atoms slow the protonation of the cluster, which, in turn, suppresses H_2 production, making the Mo variant the most efficient.

An improved high-resolution crystallographic analysis (1.16 Å) of dithionite-reduced *A. vinelandii* MoFe protein[253] suggests the presence of a hexacoordinate light atom, thought to be nitrogen, within the FeMo cofactor cluster bonded to each of 6 Fe atoms. While these findings have been disputed,[254] a density functional theoretical study offers support for this assignment.[255] Key structural and mechanistic studies such as these, together with the P-cluster inorganic core synthesis generated by a self-assembly reaction of Fe(II) bis-amide, tetramethylthiourea, 2,4,6-triisopropylbenzene-thiol, and elemental (S_8) in a ~28% yield[256] and the demonstration that a monomolybdenum center, enclosed in an organoligand construct designed to restrict metal-core access to all but small reactants (e.g., N_2 and H^+), can generate NH_3 in a ~63−66% yield, with the Mo-center cycling through the Mo(III)−Mo(VI) states,[257] and may indicate that this enzyme is, reluctantly, ready to reveal more details of its catalytic skills.[258] Biomimetic,[259] mechanistic,[260] density functional,[261] crystal structure,[262] and protein maturation[263] studies are slowly unraveling the secrets of this very ancient and complex enzyme.

In a recent discovery with profound implicatons, a hyperthermophilic methanogenic Archaeon, called FS406-22, that can reduce N_2 to NH_3 at ~90−92 °C, has been discovered some 1500 m below sea level in a hydrothermal vent in the Northeast Pacific Ocean Juan de Fuca Ridge area. It is proposed that, among the diazotrophic archaea, the nitrogenase from FS406-22 might have retained the most ancient characteristics, possibly derived from a nitrogenase present in the last common ancestor of modern life.[264]

6.5.2. Nitrosomonas Europaea. A Minimalist Organism Candidate?

An unraveling of the complete genomic sequence of *Nitrosomonas europaea*, a bacterial chemolithoautotroph, using CO_2 and NH_3 as its only sources for metabolic carbon and energy,[265] provides fascinating insight into what may be a candidate for a "minimalist organism" register. The *N. europaea* genome consists of a single circular chromosome of some 2.8 million base pairs (Mbp) encoding for fewer than 2,500 proteins. By the successive action of two of these

proteins, ammonia monooxygenase (AMO) and hydroxylamine oxidoreductase (HAO), NH_3 is converted to NO_2^-

$$NH_3 + O_2 + 2H^+ + 2e^- \rightarrow NH_2OH + H_2O \rightarrow$$
$$NO_2^- + 5H^+ + 4e^- \quad (24)$$
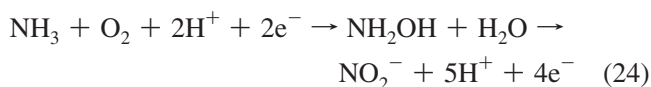
Two of the four electrons return to the AMO reaction, and two are either reductant for biosynthesis or pass to a terminal electron acceptor.

The discovery of marine and soil crenarchaoeta[266] that can oxidize NH_3 to NO_2^-,

$$NH_3 + 1.5O_2 \rightarrow NO_2^- + H_2O + H^+$$
$$(\Delta G^\circ = -235 \text{ kJ mol}^{-1}) \quad (25)$$
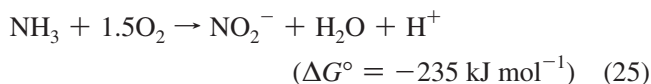
(ref 266a), the first observation of nitrification in the Archaea, suggests that these organisms may be the dominant players in an extremely dynamic $NH_3/NO_3^-/NO_2^-$ cycle in oceanic and soil ecosystems and raises numerous questions. Among them: Did NH_3 oxidation originate within the bacteria or archaea, or both?

Complex metabolic processes abound in these relatively "simple" organisms. The presence of a large battery of cytochromes in *N. europea* points to a high dependency on iron acquisition. Receptors for (>20) different Fe-receptor siderophores (extracellular Fe-binding compounds that mediate iron transport into cells) are encoded. However, but for one exception (a citrate transporter), biosynthetic pathways for siderophores were absent. *N. europaea* may rely on other bacteria to produce siderophores and then use an arsenal of receptors to harvest their products. Recent evidence based on crystal structure analysis suggests that methanobactin, a small copper-chromopeptide from the methanotrophic bacteria *Methylosinus trichosporium* OB3b, may function as a "copper siderophore" or "chalcophore" (Greek for copper) in CH_4-oxidizing bacteria.[267]

By way of comparison, *Nanoarchaeum equitans*, with a size of some 0.490 Mbp, may be the product of reductive evolution or a "primitive" archaeal ancestor. These hyperthermophiles lack the genes for central metabolism and grow only in culture only with another Archaeon, *Ignicoccus* sp., indicative of a symbiotic and parasitic relationship, representing the new archaeal kingdom, Nanoarchaeota. The complexity of its information processing systems and simplicity of its metabolic apparatus points to an unanticipated world of new organisms awaiting discovery.[268]

The size and complexity of the newly discovered nucleo-cytoplasmic DNA Mimivirus (for Mimicking microbe), *Acanthamoeba polyphaga Mimivirus*, the largest known virus sequenced to date,[269] with its unprecedented number of enzymes and putative metabolic pathways encoded by its 1.2 Mbp genome, blurs the established frontier between viruses[270] (e.g., *Acidianus*, two-tailed archaeal virus or ATV, Häring et al., 2005) and parasitic cellular organisms with small deficient genomes (e.g., *N. equitans*) and again raises the question, are viruses alive? Viruses constitute the greatest genetic diversity in the ocean and are major players in the global geochemical cycles.[271]

6.5.3. The Anammox Reaction

A new dimension has been added to our conventional picture of the denitrification phase ($NO_3^- \rightarrow NO_2^- \rightarrow N_2$) of the overall nitrogen cycle.[272] In regions as diverse as Golfo

Dulce in Costa Rica and the Black Sea (a model for both modern and ancient anoxic environments), NH_3, produced by SO_4^{2-} reduction in marine sediments[273] diffusing upward from deep anoxic water, is consumed below the oxic zone in an anammox (anaerobic ammonium oxidation) reaction by bacteria of the order Planctomycetales, able to directly oxidize NH_3 to N_2, using nitrite as the electron acceptor

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \quad (26)$$
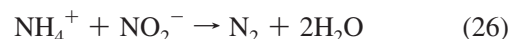
This reaction occurs in an intracytoplasmic compartment, the anammoxosome, containing unprecedented "ladderane" lipid molecules (made up of linearly fused cyclobutane moieties with cis ring junctions)[274] which make up a substantial part of the membrane structure.[275] It is proposed that such a unique (and denser) membrane structure could contain the toxic anammox reaction intermediates (N_2H_4 and NH_2OH) in the anammoxosome and help maintain concentration gradients during the slow anammox metabolism. Overall, anammox may account for between 30% and 50% of the N_2 production in the oceans. If confirmed, these[276] and more recent findings[277] may necessitate a quantitative reassessment of our understanding of the marine N_2 budget.

6.6. AOM (Anaerobic Oxidation of Methane)

6.6.1. The CH_4/SO_4^{2-} Connection

There is a general consensus that the low O_2 conditions dominating Earth's surface during the first ~2.0 Gyr of our planet's history favored the proliferation of sulfate-reducing organisms and they, in conjunction with carbon metabolizers, controlled their environment. This implies that a single process—bacterial sulfate reduction—has been in operation from the early Archaean Aeon until today.[278]

CH_4, a potent greenhouse gas, is found in copious deposits buried deep in anoxic marine sediments, frequently as methane hydrate crystals.[279] Yet very little methane from this vast reservoir escapes. The anaerobic oxidation of methane (AOM) in anoxic marine sediments off the coast of Oregon (and elsewhere) may be carried out by a consortium of archaeal CH_4 consumers (methanotrophs) and sulfate reducing bacteria (SRB).[280] In this exchange of metabolites between partners, or syntrophy, the "reverse methanogenesis" reaction, catalyzed by CH_4-consuming archaea,

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \quad (27)$$
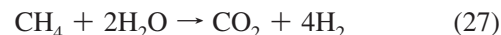
is energetically facilitated by hydrogen removal, mediated by H_2-oxidizing SRB

$$H^+ + 4H_2 + SO_4^{2-} \rightarrow HS^- + 4H_2O \quad (28)$$
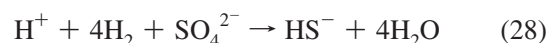
to give the overall reaction

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O \quad (29)$$
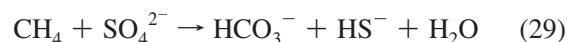
A variety of physical methods and genome-based observations were applied to microbial cell aggregates recovered from marine sediments at methane seeps in the Eel River basin in California.[281] These analyses revealed a microbial community structure dominated by SRB and ANME-1, ANME-2 (anaerobic CH_4-oxidizing *Archaea*) groups. The cell aggregates, binding a specific archaeal probe (ANME-1 or ANME-2) in their inner core, and a SRB probe on their

periphery were characterized by extremely depleted carbon, with $\delta^{13}C$ values as low as $\sim 96\%$, pointing to CH_4 as the only plausible source of carbon. The presence of genes that typify CH_4 production in methanotrophic *Archaea* provides new insight into the evolution, ecological roles, and diversity of methane-cycling *Archaea* and their unique metabolic machinery.

At methane seeps in anoxic waters of the Black Sea, massive microbial mats covering ~ 4-m high carbonate mounds are produced by a consortia of methanotrophic archaea and SRB. Here, alkalinity favors the precipitation of methane-derived bicarbonate, following the reaction

$$CH_4 + SO_4^{2-} + Ca^{2+} \rightarrow CaCO_3 + H_2S + H_2O \tag{30}$$
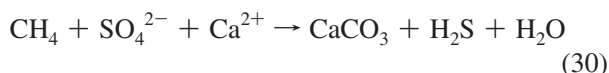
Recent studies suggest that sulfate reduction was already prolific ~ 3.5 Gya, close to the first occurrence of microfossils (~ 3.5 Gya) and the first isotopic traces of bioorganic carbon cycling (~ 3.8 Gya). Hence, AOM may have represented an important link in the biological cycling of carbon in an anoxic biosphere.[282] These microbial mats were found to contain a nickel compound (as part of an abundant protein) showing the same absorption spectrum as the Ni cofactor F_{430} of methyl-coenzyme M reductase, the terminal enzyme of methanogenesis.[283] While the Black Sea is far removed from the Pacific Ocean, these regions may share much in common metabolically. Enantiomeric bias toward compounds we associate with metabolic functionality (e.g., L-amino acids) has been established in deep-sea hydrothermal subvent fluids from a microbial oasis located in the vicinity of the Suiyo Seamount in the western Pacific Ocean.[284]

About -20 kJ mol^{-1} is a consensus estimate of the minimum energy that can be exploited by living cells. How this need is apportioned between the growth phase and "maintenance mode" for microbial populations remains to be established. The total energy available for AOM under most environmental conditions would generally be insufficient to support two organisms with a -20 kJ mol^{-1} growth energy requirement. However, biochemical catalysis of AOM by an established consortium would carry a significantly lower energy requirement.[285]

The structured archaeal−bacterial symbiosis, or metabolic exchange between partners, may not be their only mode of mutual cooperation. Methanogenic and sulfate reducing Archaea and methylotrophic bacteria have in common an energy metabolism based on the interconversion of C_1 compounds. This is in spite of the large evolutionary distance between Archaea and Proteobacteria.[286] To account for this tight metabolic functionality, it is suggested that the genes encoding these enzymes have either been conserved or transferred horizontally between more recent ancestors.

A global perspective on the sulfate/methane interaction has been provided[287] using a compilation and analysis of sedimentary pore water chemical data from the Deep Sea Drilling Project (DSDP) and Oceanic Drilling Program (ODP). The continuously high SO_4^{2-} concentrations and low CH_4 concentrations of open-ocean sites indicate that rates of sulfate reduction and methane production are very low in subsurface open-ocean sediments. In contrast, the general absence of SO_4^{2-} below a few tens of meters beneath the sea floor (mbsf) at ocean-margin sites indicated that the rate of subsurface SO_4^{2-} reduction is high relative to the rate of downward SO_4^{2-} diffusion in ocean-margin sediments. The

absence of high CH_4 concentrations in the shallowly buried sulfate-rich zone of ocean-margins sites suggests that subsurface sulfate-reducing methane oxidation is the primary means of CH_4 destruction throughout the world's oceans.

In a variation on the SO_4^{2-}/CH_4 theme, one group,[288] using small-subunit ribosomal analysis (SSU-rRNA), have identified a diversity of SRB in a biofilm community collected from a flooded tunnel within carbonate rocks in Wisconsin. These SRB, from the family *Desulfobacteriaceae,* were able to concentrate Zn as ZnS (sphalerite) within biofilm aggregates to some 10^6 times that of the associated groundwater: Zn $\rightarrow$ biofilm aggregates $\rightarrow$ ZnS. Here it is suggested SRB may use organic products of nearby communities of iron-oxidizing autotrophs or surface-derived organic inputs as substrates. If the carbon is of methanogenic origin, then a minimal equation can be written for the Zn $\rightarrow$ ZnS transformation,

$$CH_4 + Zn + SO_4^{2-} \rightarrow ZnS + CO_2 + 2H_2O \tag{31}$$
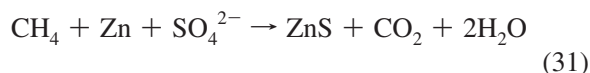
Entry of SO_4^{2-} into sulfur metabolism requires that it be chemically activated. This is accomplished by transferring the adenylyl moiety ($\sim$AMP) of ATP from pyrophosphate to SO_4^{2-} to form adenosine 5'-phosphosulfate

$$ATP^{4-} + SO_4^{2-} \leftrightarrow APS^{2-} + P_2O_7^{4-} \tag{32}$$

(i.e., activated SO_4^{2-} or APS). However, the remarkably high energy of the resulting phosphoric−sulfuric acid anhydride ($\Delta G^{\circ\prime}_{hydrolysis} \sim -19$ kcal/mol) is offset by the unfavorable equilibrium ($K_{wq} = 1.1 \times 10^{-8}$). For *E. coli* K-12 the problem is apparently solved by a multifunctional protein complex using the cysteine biosynthetic enzymes: ATP sulfurylase and O-acetylserine sulfhydrylase.[289] Since the majority of sulfur in living organisms is present in the reduced form of organic thiols, inorganic sulfate is reduced and incorporated into bioorganic compounds in an assimilatory sulfate reduction pathway.[290] By inference, these results argue strongly to the presence of APS and an ATP sulfurylase, or its catalytic equivalent, in SRB.

6.6.2. And the $CH_4/NO_3^-/NO_2^-$ Connection

Of profound significance is the recent discovery of a microbial consortium consisting of two microorganisms, a bacterium representing a phylum without any cultured species, and an Archaeon distantly related to marine methanotrophic Archaea. This "ecological guild", from the anoxic sediment of a canal in The Netherlands, has been shown to couple AOM to denitrification, growing on methane and nitrate (or nitrite) as the sole energy sources

$$5CH_4 + 8NO_3^- + 8H^+ \rightarrow 5CO_2 + 4N_2 + 14H_2O \tag{33}$$

$$3CH_4 + 8NO_2^- + 8H^+ \rightarrow 3CO_2 + 4N_2 + 10H_2O \tag{34}$$
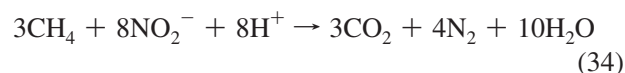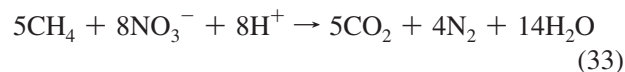
(with $\Delta G^{\circ\prime}$ values of -765 and -928 kJ mol^{-1} CH_4, respectively).[291]

6.7. The HPO_3^{2-}/SO_4^{2-} Connection

Phosphorus is known to be both scarce and ubiquitous in the Universe.[292] In what may be a first illustration of a redox

reaction involving phosphorus in microbial energy metabolism, a SO_4^{2-}-reducing bacterium, isolated from sediments of the Canale Grande in Venice, has demonstrated the unusual capacity to oxidize phosphite ion in a reaction,

$$4HPO_3^{2-} + SO_4^{2-} + H^+ \rightarrow 4HPO_4^{2-} + HS^- \quad (35)$$
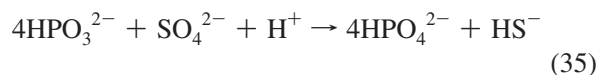
where $\Delta G^{\circ\prime} = -91$ kJ mol^{-1} of HPO_3^{2-} or -364 kJ mol^{-1} of sulfate.[293] 16S-rRNA analysis of this anaerobic strain (FiPS-3) reveals strong sequence similarities with a subclass of sulfate-reducing Proteobacteria. Microorganisms of this genre could have thrived on a litho(auto)trophic metabolism involving the oxidation of reduced phosphorus compounds, in which case, dissimilatory phosphite oxidation by SO_4^{2-} reducing bacteria may represent an ancient evolutionary trait.

Though scarce and ubiquitous, what is the source of reactive phosphorus (P), a requirement for the formation of P-based life? Inorganic polyphosphate, generated by dehydration of orthophosphate at elevated temperatures, is found in volcanic condensates and deep oceanic steam vents. In prebiotic evolution, it could have provided a flexible, polyanionic scaffold to assemble macromolecules.[294] Or did it arise from corrosion of the meteoritic mineral schreibersite ((Fe, N)3P)? Corrosion of synthetic schreibersite in a variety of solutions was analyzed by several spectral methods. These methods suggest a free radical reaction pathway for the corrosion of schreibersite to form phosphite radicals in aqueous solution. These radicals can form activated polyphosphates and can phosphorylate organic compounds such as acetate to form phosphonates and organophosphates.[295]

7. The Rise of O_2

7.1. From Anoxic to Oxic

The advent of oxygenic (oxygen-evolving) photosynthesis

$$CO_2 + 2H_2O \rightarrow [CH_2O] + H_2O + O_2 \quad (36)$$

is one of the central events in the development of life on earth as we know it.[296] This process (where CH_2O is a generic descriptor for organic biomass) lies at the core of the global biogeochemical carbon cycle. Recent evidence points to the first-rise of atmospheric oxygen probably occurring ~2.32 Gya, based on sulfur isotope measurements from organic-rich shales of the Roolhoogte and Timeball Hill formations, South Africa.[297] The presence of bacteriohopanepolyols (BHPs, e.g., 2methylhopanoids), a signature lipid of cyanobacteria, recovered from molecular fossils taken from 2.7 billion year old late Archaean kerogenous shales at depths of ~200 m in the Pilbara Craton, in 2.5 billion year old rocks in the Hammersley Basin, both in Western Australia (see section 4.6) and in Yellowstone National Park, USA, may point to the existence of oxygenic photosynthesis some 2.7−2.5 Gya. In fact, purple bacteria have been assigned a claim as the earliest emerging photosynthetic lineage with cyanobacteria-based chlorophyll−a biosynthesis occurring as a recent development in the course of evolution of photosynthetic pigments, which could have occurred by a shortening of the bacteriochlorophyll biosynthetic pathway.[298]

7.2. Why the Gap?

Against this background the question has been raised: Why was there a gap of some 400 million years (~2.7 → 2.3 Gya)

between the emergence of cyanobacteria and the rise of atmospheric O_2?[299] A key to the paradox of low-level solar luminosity and temperate Archaean climate[300] may lie in the greenhouse gas effect of CH_4.[301] In an update to the Archaean CH_4 greenhouse warming theory, a biogeochemical mechanism tied to Earth's redox history has been proposed.[302] Initially, H in the organic matter (CH_2O) generated by oxygenic photosynthesis (eq 36) is transformed into methane by (i) the symbiotic communities of methanogens and heterophiles decomposing organic matter

$$2CH_2O = CH_4 + CO_2 \quad (37)$$

followed by photolytic decomposition of CH_4 in the upper atmosphere by ultraviolet radiation

$$CH_4 + h\nu \rightarrow C + 4H(\uparrow space); C + O_2 = CO_2 \quad (38)$$
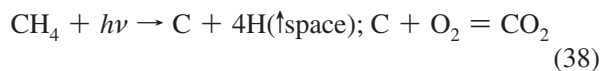
The resulting irreversible loss of H in this overall reaction sequence (eqs 36*2 + 37 + 38) leads to an irreversible gain of O_2.

$$2H_2O + \text{"the biopshere"} + h\nu \rightarrow O_2 + 4H(\uparrow space) \quad (39)$$
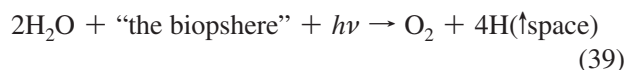
CH_4 may have been available from sources other than (i). These include (ii) anoxygenic photo- or chemoautotrophic metabolism, where (Fe^{2+}) or reduced S

$$2H_2S + CO_2 - h\nu \rightarrow CH_2O + H_2O + 2S \quad (40)$$
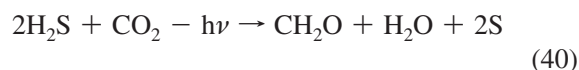
or (iii) mantle H_2 in volcanic gases could serve as an electron donor in methanogenic biosynthesis

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \quad (41)$$
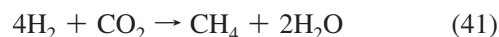
In case (ii), H escape would leave behind oxidized S (or Fe), contributing to net crustal oxidation. In fact, large O_2 inventories reside in the continental crust and mantle, sequestered in altered and metamorphosed igneous rocks.

Sedimentary evidence from the 3.416 Gy-old Buck Reef Chert (BRC) in South Africa—where matlike organic (carbonaceous) laminations in banded chert deposited in a shallow marine environment at a depth to which light could penetrate the water column (the euphotic zone)—points to the presence of an active anoxygenic photosynthetic community

$$Fe^{2+} + CO_2 + H_2O \rightarrow FeCO_3 + 2H^+ \quad (42)$$
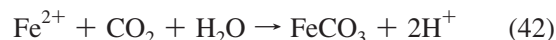
in a 3.4 Gy-old Archaean ocean. These results are based on the carbon isotope composition of BRC carbonaceous matter, the presence of siderite ($FeCO_3$) and lack of primary ferric oxides, and the restriction of microbial mats to shallow water within the euphotic zone, subsequently distributed as detrital matter by waves and currents to surrounding environments.[303]

Given the distribution of O_2 in the Archaean atmosphere and mantle, and the propensity of vanadium to exist in multivalent states (V^{+3}, V^{4+}, V^{5+}) in melts at terrestrial oxygen fugacity (fO_2), studies were undertaken to unravel the paleo-redox states during formation of mantle lithosphere using the vanadium(V) abundances of peridotites. These results suggest the mantle was oxidized early (by ~3.5 Gya), so gradual oxidation of the solid Earth system by volcanic

degassing of reducing species and ensuing H_2 escape cannot have occurred. It is suggested that future models for prebiotic synthesis and the evolution of O_2 in the atmosphere must consider a more oxidative state of the Archaean mantle.[304]

7.3. Prochlorococcus and Synechococcus

About one-half of global photosynthesis and O_2 production is carried out by phytoplankton (unicellular marine cyanobacteria), two genera of which (*Prochlorococcus* and *Synechococcus*) may account for as much as two-thirds of the marine CO_2 production and nearly one-third of the primary biomass production on Earth.[305,306] Sequence and analyses of the complete genome of one strain (WH8102) of *Synechococcus*[307] and three strains of *Prochlorococcus* (MED4, MIT9313, SS120)[308,309] offer profound insight into their molecular makeup and strategies for coping with hostile environments.

Because *Prochlorococcus* is an O_2-evolving photolithoautotroph, it must have the ability to synthesize all cellular constituents, including amino acids, nucleotides, coenzymes, etc., from CO_2 and mineral salts. It must also encode all the proteins and required cofactors for oxygenic syntheses (e.g., chlorophyll, carotenoids, quinones, heme, the photosynthetic electron transport chain and light harvesting proteins, and the Calvin cycle). Given its small physical and genomic size, some metabolic functionalities are missing or less diversified. These "deficiencies" include (but are not limited to) the inability to utilize NO_3^-, NO_2^-, urea, and cyanate as nitrogen sources; genes for siderophore (iron-loving) production; and some DNA repair systems.[308,309]

The several strains of *Prochlorococcus* that have been sequenced occupy different habitats in tropical and temperate oceanic ecosystems. A high-light-adapted genotype (MED4) occupies the upper, well illuminated, but nutrient-poor 100 m layer of the water column. In contrast, the low-light adapted genotypes (MIT9313 and SS120) thrive best in the lower levels of the euphotic zone (80−200 m), a nutrient-rich but dimer-light environment. Their tiny cell size (0.5−0.7 μm diameter) and genomic makeup, in terms of millions of base pairs (SS120, 1.75 Mbp; MED4, 1.66 Mbp; MIT9313, 2.41 Mbp) qualify them as the smallest photosynthetic organisms known to date.[309] By comparison, the red algae, *Cyanidioschyzon merolae* 10D, an unicellular organism that inhabits sulfate-rich hot springs (pH 1.5, 45 °C), has the smallest genome of all photosynthetic eukaroytes (2 μm diameter, ~16.52 Mbp).[310]

MIT9313 has adaptations that seem to place its optimum depth between MED4 and SS120 in the water column The enhanced genomic versatility embedded in its larger genome may enable MIT9313 to exploit the diverse resources of this "transition" zone where it lives.[308] The *pcb* genes, encoding the major chlorophyll-binding, light-harvesting antenna proteins in this genus, are present in multiple copies in low-light strains, but as a single copy in high-light strains.[311] The markedly different distributions among these strains within a stratified water column occur in spite of the fact that they differ in their rDNA sequence by less than 3% and would be lumped together as a single species on the basis of their rDNA similarity.[308] As this group points out, it may be useful to view *Prochlorococcus* and *Synechococcus* as important "minimal life units", as the information in their roughly 2,000 genes is sufficient to create globally abundant biomass from solar energy and inorganic compounds. More recent studies confirm and extend the pervasive distribution of Prochlo-

roccous in both vertical and horizontal pelagic environments, facilitated perhaps by the presence of acquired "guest" genes (phages?), each uniquely suited to its particular niche environment.[312]

It cannot be assumed that the rise of O_2 was evenly and rapidly distributed across all components of our biosphere.[313] Increasing atmospheric O_2 levels could have triggered a sequence of reactions leading to a more suphidic ocean.[314] Studies of Mo and S isotope data from modern and ancient deep ocean sediments indicate that the latter remained euxinic (i.e., anoxic and sulfidic) well into the mid- or late-Proterozoic Aeon. Deep ocean oxygenation may have lagged atmospheric oxygen build-up by over 10^9 years.[315]

The evolution of oxygenic photosynthesis marks the dawn of oxidative stress, one of the greatest selective pressures imposed on primordial life with the generation of reactive oxygen species (ROS, e.g., O_2^-, H_2O_2, $HO^\bullet$).[316] In this connection, the aerobic hyperthermophilic Archaeon, *Sulfolobus solfataricus* (Ss), was shown to contain a Dps-like protein, SsDps, that functions as a Dps (DNA-binding protein from nutrient-starved cells). Unlike the Fenton reaction

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^\bullet \quad (43)$$
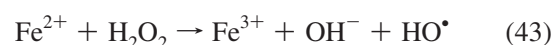
which generates the toxic hydroxyl radical, the ferroxidase center in Dps proteins uses $Fe^{2+} + H_2O_2$ more efficiently

$$2Fe^{2+} + H_2O_2 + 2H_2O \rightarrow 2Fe(O)OH_{(s)} + 4H^+ \quad (44)$$
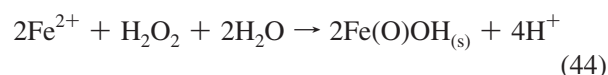
in a mineralization reaction to avoid oxidative damage. Apparently, these ancient organisms harbored molecular mechanisms sufficient to cope with oxidative stress.

Solar radiation may not be the *sine qua non* of all photosynthetic organisms.[317] Water samples collected from several East Pacific Rise deep sea hydrothermal vents, where the only source of light is geothermal radiation (a photon flux at ~750 ± 50 nm), were cultured in appropriate medium. Illumination gave rise to a green-pigmented turbidity attributed to a small, nonmotile green sulfur bacterium (GSB1). Numerous other collected samples failed to yield microbial growth in this enriched medium.

7.4. From H_2O to O_2 and NADPH: Filling in the Details

Recent developments in refined crystal-structure analysis on PsII (photosystem II) and cytb$_6$f (the Cytochrome b_6f complex) have given us the first complete picture of the molecular events of oxygenic photosynthesis.

PS II

A refined structural analysis of the PSII enzyme (water-plastoquinone photo-oxidoreductase) from the cyanobacterium *Thermosynechococcous elongatus* at 3.5 Å resolution reveals the presence of five metal ions in the oxygen-evolving center (OEC), four of them Mn and the fifth, probably Ca, with a cubane-like Mn_3CaO_4 cluster and a mono-μ-oxo bridge to the fourth Mn ion. This enzyme uses solar energy to drive the reduction of plastoquinone at the start of the photosynthetic electron-transfer chain using electrons stripped from water and generating O_2 as a "waste" product[318] and the hydroxyl radical ($OH^\bullet$), produced on the electron acceptor side of PSII by two different routes.[319]

Cytochrome b_6f

Two groups, working independently, have resolved the structure of cyt b_6f, in one case from an unicellular alga, *Chlamydomonas reinhardtii,* at 3.1 Å resolution,[320] and, in the other, from the cyanobacterium, *Mastigocladus luminosus*, at 3.0 Å resolution.[321] Cytb$_6$f, a dimer with two identical sets of components, has several membrane-spanning proteins including cytochromes *c* and *f*, and an Fe−S cluster protein, plus pigment molecules including four hemes, a chlorophyll, and a *β*-carotene. Both complexes from these disparate sources have essentially the same structure, which in itself is astonishing, since the two types of organisms are separated by an evolutionary distance of some 10^9 years.[322]

7.5. The Linear Electron Flow: PSII $\rightarrow$ Cyt b_6f $\rightarrow$ PSI

In outline,

$$H_2O + -h\nu, \text{PS II, PQ} \rightarrow$$

$$^1/_2O_2 \uparrow +PQH_2 - PQ, \text{cyt } b_6\text{f, PC} \rightarrow \text{PC}$$

$$\text{PC} - h\nu, \text{PSI(Fd, FNR, NADP}^+) \rightarrow \text{NADPH}$$
(45)
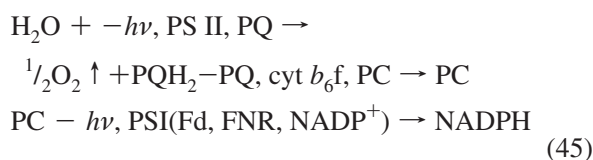
two electrons (and protons) stripped from a water molecule by radiant energy at the PSII reaction center are accepted by plastoquinone (PQ), generating reduced plastoquinone, PQH$_2$ (and oxygen as a "waste" product). PQH$_2$ diffuses in the membrane to the cyt b_6f complex, where one electron is transferred to plastocyanin (PC) and the other electron is passed to another PQ molecule. PC, in turn, diffuses to PS I (photosystem I), which uses solar energy to propel the electron against a potential gradient across the membrane, where it is accepted by ferrodoxin (Fd) and transferred to FNR (ferredoxin/NADP$^+$ oxidoreductase), reducing NADP$^+$ to NADPH, the primary product of photosynthesis.[322]

The wealth of structural detail revealed from these and additional studies[323] should help us to better understand the mechanistic and catalytic nuances of these very complex and integrated reaction sequences found among some of the most primitive of organisms.

8. Concluding Remarks

What is strikingly evident across the prebiotic world, whether interstellar or planetary, is the innate capacity of matter and energy to carry out covalent bond synthesis, self-assembly, and self-organization. Components of any size, from molecules to galaxies, can self-assemble in a permissive environment. Baryonic (ordinary) matter contributes only ∼4−5% to the total energy density of the Universe. The remainder is attributed to dark matter (∼23%) and dark energy (∼70%).

The antiquity of the genetic code is evident from its distribution. Archaea, Bacteria, and Eukarya use the same set of codon assignments, indicating the code predates their divergence on the ring or tree of life. *Nanoarchaeum equitans*, with the smallest microbial genome sequenced to date (0.490 Mbp), may be a primitive archaeal ancestor or the product of reductive evolution. These submarine vent hyperthermophiles lack the genes for central metabolism and grow only in coculture with another Archaeon, *Ignicoccus* sp., indicative of a symbiotic and parasitic relationship, representative of a new archaeal kingdom, Nanoarchaeota.

The complexity of its information processing systems and simplicity of its metabolic apparatus point to an unanticipated world of new organisms awaiting discovery. A genomic comparison of *N. equitans* with the nucleocytoplasmic DNA Mimivirus, the largest known virus sequenced to date, with its unprecedented number of enzymes and putative metabolic pathways encoded by its 1.2 Mbp genome, blurs the established frontier between viruses and parasitic cellular organisms and raises again the question, are viruses alive? It may be useful to view *Prochlorococcus and Synechococcus* as important "minimal life units", as the information in their roughly 2,000 genes is sufficient to create globally abundant biomass from solar energy and inorganic compounds. It cannot be assumed that the rise of O$_2$ was evenly and rapidly distributed across all elements of the biosphere. Increasing atmospheric O$_2$ levels could have triggered a sequence of reactions leading to a more sulphidic ocean. Deep ocean sediments may have remained euxinic (i.e., anoxic and sulphidic) and lagged atmospheric oxygen buildup well into the midor late-Proterozoic Period.

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