

1 **Fundamental Molecules of Life are UV/VIS Pigments which** 2 **Arose and Evolved as a Result of their Solar Spectrum** 3 **Dissipating Efficiency**

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10 11 **Abstract**

12 The driving force behind the origin and evolution of life has been the thermodynamic
13 imperative of increasing the entropy production of the biosphere through increasing the
14 global solar photon dissipation rate. In the upper atmosphere of today, oxygen and
15 ozone derived from life processes are performing the short wavelength UV-C and UV-B
16 dissipation. On Earth's surface, water and organic pigments in water facilitate the near
17 UV and visible photon dissipation. The first organic pigments probably formed,
18 absorbed, and dissipated at those photo chemically active wavelengths in the UV-C and
19 UV-B that could have reached Earth's surface during the Archean. Proliferation of these
20 pigments can be understood as an autocatalytic photochemical process obeying non-
21 equilibrium thermodynamic directives related to increasing solar photon dissipation
22 rate. Under these directives, organic pigments would have evolved over time to increase
23 the global photon dissipation rate by; 1) increasing the ratio of their effective photon
24 cross sections to their physical size, 2) decreasing their electronic excited state life
25 times, 3) quenching radiative de-excitation channels (e.g. fluorescence), 4) covering
26 ever more completely the prevailing solar spectrum, and 5) proliferating and dispersing
27 to cover an ever greater surface area of Earth. From knowledge of the evolution of the
28 spectrum of G-type stars, and considering the most probable history of the transparency
29 of Earth's atmosphere, we construct the most probable Earth surface solar spectrum as a
30 function of time and compare this with the history of molecular absorption maxima
31 obtained from the available data in the literature. This comparison supports the
32 conjecture that many fundamental molecules of life are pigments which arose,
33 proliferated, and evolved as a response to dissipating the solar spectrum, supports the
34 thermodynamic dissipation theory for the origin of life, constrains models for Earth's
35 early atmosphere, and sheds some new light on the origin of photosynthesis.

36 37 **1. Introduction**

38 Like all irreversible processes, life must have arisen because it was effective at
39 dissipating a generalized thermodynamic potential. By far the most important potential
40 that life dissipates today is the solar photon potential. Living systems reduce the albedo
41 of Earth and dissipate, through many coupled irreversible processes, shortwave
42 incoming radiation into long-wave radiation which is eventually returned to space,
43 ensuring an approximate energy balance in the biosphere. We have suggested that the
44 optimization of this entropy production under the solar photon potential provides the
45 motive force behind the origin and evolution of life (Michaelian, 2005; 2009; 2011;
46 2012a; 2012b; 2013).

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48 Many of the earliest organic molecules, those common to all three domains of life
49 (Bacteria, Archaea and Eukaryote), are pigments which absorb light in the middle

50 ultraviolet (UV-C and UV-B) and when in an aqueous environment dissipate this light
51 efficiently into heat. (The word “pigment”, as used here, refers to a molecule that
52 selectively absorbs at any wavelength, not only in the visible.) Over the history of life
53 on Earth, organic pigments have evolved because they absorb in the range where water
54 does not, approximately 220 to 700 nm. Stomp et al. (2007) have, in fact, demonstrated
55 just how neatly organic pigments are filling photon niches left by water. From this
56 thermodynamic perspective, the origin of life began with the photochemical formation
57 of organic pigments that dissipate the solar photon potential arriving at Earth's surface
58 where water does not absorb. Specifically, we have postulated (Michaelian, 2009, 2011)
59 that life began dissipating UV-C photons within the range of 240 nm to 280 nm, where
60 a window existed in the primitive Earth atmosphere (Sagan, 1973) and where the
61 primary molecules, those common to all three domains of life (RNA and DNA, the
62 aromatic amino acids, and enzymatic cofactors) absorb and dissipate strongly when in
63 water.

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65 This "thermodynamic dissipation theory for the origin of life" suggests that the
66 evolutionary trajectory of life on Earth is, and always was, driven by increases in the
67 global photon dissipation rate of the biosphere. This is obtained through optimizing the
68 pigment photon dissipation at the entropically most important photon wavelengths
69 (short wavelengths) arriving at Earth's surface by evolving; 1) increases in the photon
70 absorption cross section with respect to pigment physical size, 2) decreases in the
71 electronic excited state life times of the pigments, 3) quenching of the radiative de-
72 excitation channels (e.g. fluorescence), 4) greater coverage of the solar spectrum, and 5)
73 pigment proliferation and dispersion over an ever greater surface area of Earth by
74 evolving mobile organisms that spread essential nutrients and seeds into inhospitable
75 environments, including mid-ocean and extreme land environments (Michaelian, 2009,
76 2011, 2012a).

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78 The earliest organic pigments on Earth's surface were probably formed directly via
79 photochemical reactions on prebiotic molecules such as H₂, N₂, CO₂, CH₄, HCN, H₂O
80 and common polycyclic aromatic hydrocarbons (Oró and Kimball, 1961).
81 Contemporary organic pigments have to be formed through more indirect biosynthetic
82 routes, since high energy photochemically active wavelengths are no longer available at
83 Earth's surface, but are still ultimately derived from photochemical reactions in the
84 visible. When in water these pigments dissipate the solar photon potential into heat and
85 their formation can therefore be viewed as an autocatalytic dissipative process driven by
86 entropy production. This non-linear, non-equilibrium process results in concentrations
87 of the pigments orders of magnitude beyond their expected equilibrium values (this has
88 been well studied for chemical reactions, Prigogine (1967), and we have extended it to
89 the photochemical reactions, Michaelian (2013)) and thus explains the proliferation of
90 organic pigments over Earth's entire surface (Michaelian, 2011, 2013).

91
92 Nucleic acid and other fundamental pigment proliferation at the beginning of life is
93 assumed to have been generated by the photochemical autocatalytic process as
94 mentioned in the previous paragraph, although the detailed mechanisms of these
95 processes are yet to be determined. Patel et al. (2015) have, in fact, found
96 experimentally plausible routes to the generation of these pigments using UV-C light.
97 RNA molecules have also been found to catalyze the synthesis of nucleotides, i.e. their
98 own building blocks (Unrau and Bartel, 1998).

99

100 We believe that a fundamental thermodynamic reason for the polymerization of these
101 nucleic acids into single strands is that they could then act as stereochemical templates
102 for the attachment of other UV-C absorbing pigment molecules (such as, for example,
103 the aromatic amino acids which have affinity to their codons or anticodons) that could
104 act as electronically excited donors to the RNA or DNA single strand polymers acting
105 as acceptors and providing rapid radiation-less dissipation of the electronic excitation
106 energy to the ground state (for example, aromatic amino acid excited state lifetimes are
107 of the order of nanoseconds whereas RNA or DNA excited state lifetimes are sub
108 picosecond). The complex of pigment+RNA/DNA would thus dissipate more UV-C
109 than the sum of its component parts.

110
111 A template-directed mechanism for the primordial non-enzymatic replication of
112 RNA/DNA, which we called UVTAR (Ultra-Violet and Temperature Assisted
113 Replication) was given in an earlier work (Michaelian, 2009, 2011). In this scenario, the
114 local heat generated by the dissipation of a UV-C photon by the nucleic acid bases of
115 RNA or DNA is sufficient to disrupt the hydrogen bonds between complementary bases
116 and allow separation into single strands. This hypothesis has been supported by recent
117 experimental data (Michaelian and Santillán Padilla, 2014) showing that short strand (<
118 48 bp) double-stranded DNA effectively denatures when exposed to UV-C light.
119 Enzyme-less extension to form a complementary strand is plausible if it were performed
120 overnight at colder sea surface temperatures and using Mg^{2+} ions as cofactors. Some
121 experimental evidence for this kind of enzyme-less extension has already been given
122 (Szostak, 2012 and references therein).

123 One could look at the overall process of production and replication of RNA or DNA in
124 terms of the individual steps or mechanisms, for example; 1) autocatalytic
125 photochemical production of the nucleic acid bases and other pigment molecules, 2)
126 polymerization of the bases into single strands, 3) attachment of other pigment
127 molecules to coding sections on the RNA or DNA polymers, 4) UV-C induced
128 denaturing, and 5) enzyme-less extension. Alternatively, one could look at the process
129 as one large autocatalytic photochemical reaction in which the net result is the
130 proliferation of specific (coding) RNA or DNA segments which have large photon
131 dissipation capacity. The latter view is a more general thermodynamic view while the
132 former view, considering the individual steps in the overall reaction, is a more detailed
133 mechanistic view. A still more detailed view of the actual mechanisms operating in each
134 step has yet to be delineated, particularly with regard to mechanisms (routes) to the UV-
135 C photochemical production of the pigments (point (1) above). However, the general
136 view of the proliferation of coding segments of RNA and DNA, as an autocatalytic
137 photochemical reaction which proceeds and evolves through thermodynamic selection
138 based on the efficacy of the organism to dissipate the solar photon potential is the most
139 useful view for providing a physical-chemical description of evolution through natural
140 selection and avoids having to include an *ad hoc* "will (drive) to survive" (the
141 Darwinian postulate) in the description of evolution.

142
143 The most general trend of evolution (the hallmark of evolution) appears to be towards
144 covering the entire surface of Earth with organic pigments. Near the beginnings of life,
145 this proliferation was attained through abiotic means (particularly using UV-C light and
146 autocatalytic dissipative photochemical reactions) while today it is carried out through
147 complex biosynthetic pathways, but still ultimately dependent on light. The net effect
148 has been the increase in photon dissipation and this is being thermodynamically selected
149 (on which natural selection must ultimately be physically grounded).

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151 Driving the proliferation and evolution of life is thus the thermodynamic imperative of
152 increasing the global entropy production of the biosphere. Since the bulk of the entropy
153 production on Earth's surface consists mainly in the dissipation of solar photons by
154 organic pigments in water, the history of absorption by organic pigments should
155 correlate with the evolution of the surface solar photon spectrum. Based on this
156 conjecture, in this article we first consider the most probable evolution of the solar
157 spectrum at Earth's surface and compare this with a pigment history (a pigment tree of
158 life) reconstructed from the available data in the literature. This comparison leads us to
159 the conclusion that many fundamental molecules of life are organic pigments, lends
160 strong support to the thermodynamic dissipation theory for the origin of life
161 (Michaelian, 2009, 2011), constrains models of Earth's early atmosphere, and sheds new
162 light on the origin of photosynthesis.

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164 **2. Evolution of Earth's surface photon spectrum**

165 From the best available knowledge of the evolution of solar type stars and of the
166 evolution of Earth's atmosphere we reconstruct here the most probable solar photon
167 spectrum reaching Earth's surface as a function of time since the beginnings of life. In
168 Sect. 4, this reconstruction is compared with the available data concerning the history of
169 pigment absorption presented in Sect. 3.

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171 **2.1 Evolution of the solar spectrum**

172 Through studying nearby spectral type G and luminosity class V (G-V-type) main
173 sequence stars similar to our Sun, of 0.8 to 1.2 solar masses and surface temperatures of
174 between 5,300 and 6,000 K, which have known rotational periods and well-determined
175 physical properties, including temperatures, luminosities, metal abundances and ages,
176 Dorren and Guinan (1994) have been able to reconstruct the most probable evolution of
177 our Sun's characteristics over time, in particular, the evolution of its spectral emission.
178 This "Sun in Time" project has been carried out using various satellite mounted
179 telescopes including ROSAT, Chandra, Hubble, and EUVE and now has representative
180 data for our Sun's main sequence lifetime from 130 Ma to 8.5 Ga.

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182 Over the lifetime of G-type main sequence stars, emitted wavelengths of shorter than
183 150 nm originate predominantly in the chromosphere and corona (stellar atmosphere) in
184 solar flares resulting from magnetic disturbances. The high rotation rate of a young star
185 gives it an initially large magnetic field, before significant magnetic braking sets in,
186 and thus intense and more frequent solar flares leading to large fluxes of these very high
187 energy photons. In Fig. 1 the short wavelength flux intensities as a function of the age
188 of a G-type star are given. From the figure it can be seen that our Sun at 500 Ma (at the
189 probable beginnings of life on Earth at 3.85 Ga), would have been 5 to 80 times
190 (depending on wavelength) more intense at these very short wavelengths.

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192 Wavelengths greater than 150 nm are known to originate on the photosphere and are
193 emitted essentially in a black-body spectrum (apart from a few strong stellar
194 atmospheric absorption lines) at the star's effective surface temperature (Cnossen et al.,
195 2007). The effective surface temperature of a star is related to its visible luminosity L_S
196 and radius r by the Stefan-Boltzmann law,

$$197 \quad T_{eff} = \left(\frac{L_S}{4\pi\sigma r^2} \right)^{1/4},$$

198 where σ is the Stefan-Boltzmann constant.

199

200 The luminosity of a star is an increasing function of its age because hydrogen fusion
201 begins predominantly in the core and gradually proceeds outwards as helium "ash"
202 settles into the core (Karam, 2003). Our Sun, at the time of the origin of life, is thus
203 expected to have been about 30% less luminous than today. The radius of a star is also a
204 monotonically increasing function of its age (Bahcall et al., 2001). The net result for our
205 Sun is that its effective surface temperature has been increasing steadily and at the
206 origin of life was approximately 1.6% less than today, while the integrated UV flux
207 (176-300 nm) was most likely about 15% less than today (Karam, 2003).

208

209 **2.2 Evolution of the transparency of Earth's atmosphere**

210 Far more uncertain, but much more important than the incident solar spectrum in
211 determining the solar photon flux at Earth's surface in prior times, is the wavelength
212 dependent extinction in the atmosphere due to both absorption and scattering. Although
213 the exact history of the primitive atmosphere and its evolution to its present state is still
214 under active debate, there are, fortunately, well established geochemical data from the
215 abiotic and biotic fossil record that constrain model scenarios.

216

217 Earth's second atmosphere of the Archean (the first atmosphere was probably lost to
218 space during the heavy asteroid bombardment of between 4.4 and 4.2 Ga with a late
219 spike in bombardment at between 3.9 and 3.8 Ga (post late-lunar bombardment; Gomes
220 et al., 2005)) is thought to have been composed mainly of N₂, CO₂, H₂O, some CH₄,
221 NH₃, with the ratio CH₄/CO₂ \ll 1 (Kasting et al., 1983; Kharecha et al., 2005), and
222 perhaps up to 0.1 bar of H₂ (Tian et al., 2005), but with very little oxygen and therefore
223 essentially no ozone. For commonly assumed Archean atmospheric pressures of around
224 1 bar, these gases are all nearly perfectly transparent above approximately 220 nm
225 (Sagan, 1973). However, considering probable volcanic out-gassing of hydrogen sulfide
226 (the most thermodynamically probable sulfur-containing gas under reducing conditions;
227 Miller, 1957; Sagan and Miller, 1960) from many active vents and the likely formation
228 rates of aldehydes (formaldehyde and acetaldehyde) through UV photochemical
229 reactions on hydrogen sulfide, Sagan (1973) calculated a 240 to 290 nm window of
230 transparency in the UV for Earth's atmosphere at the beginning of life. The two above
231 cited aldehydes would have caused strong extinction from 290 nm to approximately 320
232 nm (Sagan, 1973).

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234 The oxygen isotope content in zircon crystals betrays the existence of liquid water on
235 Earth's surface since well before the beginning of life (Mojzsis et al., 2001). However,
236 as stated above, the standard solar model and observational data on stars similar to our
237 Sun suggest that the wavelength integrated luminosity of our Sun was as much as 30%
238 less at the beginnings of life (Sagan and Chyba, 1997) which is inconsistent with the
239 presence of liquid water unless one accepts a strong greenhouse atmosphere or a very
240 different evolutionary model for our Sun; such as an early high mass loss rate (Guzik et
241 al., 1987) or a pulsar centered Sun (Michaelian and Manuel, 2011). The most probable
242 greenhouse gases are carbon dioxide, water vapor, methane, and ammonia. Lowe and
243 Tice (2004) have presented geologic data suggesting that the Earth was kept warm by
244 CO₂ and CH₄ at ratios of CH₄/CO₂ \ll 1, maintaining surface temperatures around 80°C
245 at 3.8 Ga (Knauth, 1992; Knauth and Lowe, 2003) and falling to 70 ± 15 °C at 3.5–3.2
246 Ga (Lowe and Tice, 2004). Ammonia is very susceptible to UV destruction and
247 therefore it is not considered to have been a major component of Earth's atmosphere
248 during the Archean (Sagan, 1973).

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Using a model based on the present spectral emission of the G-V star κ^1 Cet (HD 20630) of an estimated age of 0.5 Ga, the age of the Sun at the beginning of life (3.95-3.85 Ga), and the Beer-Lambert law for atmospheric absorption but without considering multiple scattering, Cnossen et al. (2007) have shown that wavelengths below about 200 nm would have been strongly extinguished by N_2 , H_2O and CO_2 in the atmosphere. In their estimation, at no time in Earth's history would its surface have been subjected to radiation shorter than 200 nm. There is, however, some contradictory evidence in mass-independent sulfur isotopic signatures, suggesting that wavelengths as short as 190 nm may have penetrated to low altitudes in the Earth's early atmosphere, at least until about 2.45 Ga (Farquhar et al., 2001).

Cnossen et al.'s (2007) calculations for the photon flux intensity at 260 nm, where RNA and DNA absorb strongly, is approximately $1 \times 10^{-2} \text{ W m}^{-2} \text{ nm}^{-1}$ (or $1.4 \times 10^{12} \text{ photons s}^{-1} \text{ cm}^{-2} \text{ nm}^{-1}$) which, although seemingly small, is roughly 10^{31} times greater than what it is today due to the absorption at this wavelength by ozone and oxygen in today's atmosphere (Cnossen et al., 2007). Considering only absorption based on the predicted amount of oxygen in the atmosphere, and the expected cross section for photochemical production of ozone, Karam (2003) has predicted a somewhat higher photon flux at 260 nm of approximately $1 \times 10^{13} \text{ photons s}^{-1} \text{ cm}^{-2} \text{ nm}^{-1}$. Sagan (1973) has calculated an integrated flux of light reaching Earth's surface of wavelength $\leq 290 \text{ nm}$ of approximately 3.3 W m^{-2} and has estimated that such a flux would be lethal to today's organisms in under 0.3 s.

Although CO_2 , H_2O and the other primordial gases would have absorbed almost all of the very high energy incident photons ($< 200 \text{ nm}$) coming from an early Sun (see Fig. 1) of age $< 0.5 \text{ Ga}$, this light still has some relevance to the spectrum at Earth's surface since some photons would have Compton scattered into energies within the atmospheric window of transparency of between 240 and 290 nm and be available at the surface of Earth for absorption by the early organic pigments. Employing calculations by Smith et al. (2004), Cnossen et al. (2007) estimate that the contribution of Compton scattered X-ray photons into an atmospheric window of 200-300 nm would have provided an additional $\sim 10^{-6} - 10^{-5} \text{ W m}^{-2} \text{ nm}^{-1}$, with the scattering of still higher energy gamma rays into the window increasing this only slightly.

Lowe and Tice (2004) have suggested a gradual depletion of atmospheric CO_2 through the carbonate-silicate geochemical cycle starting around 3.2-3.0 Ga through weathering of the newly forming continental crust, including the Kaapvaal and Pilbara cratons. By 2.9-2.7 Ga, CH_4/CO_2 ratios may have become ~ 1 thereby stimulating the formation of an organic haze that would have given rise to a large visible albedo and reducing surface temperatures to below 60°C at 2.9 Ga, perhaps allowing oxygenic photosynthetic organisms to thrive and increasing the amount of oxygen and ozone in the atmosphere (Lowe and Tice, 2004). Pavlov et al. (2000) have shown that 1,000 ppmv each of CH_4 and CO_2 (Kharecha et al., 2005) would counteract the faint young Sun sufficiently to keep temperatures above freezing at this time. However, not all of Earth may have remained above freezing since glacial tillites have been identified in the $\sim 2.9 \text{ Ga}$ Pongola and Witwatersrand Supergroups of South Africa (Young et al., 1998; Crowell, 1999). Eventual erosion of the continents and tectonic recycling of CO_2 would have allowed the CH_4/CO_2 ratio to reduce again, bringing back a warm greenhouse atmosphere to the late Archean.

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300 Using as a model the results obtained from the Cassini/Huygens mission for Titan,
301 Trainer et al. (2006) have investigated the probable formation of organic haze on an
302 early Earth through photolysis of CH₄ with the solar Lyman- α line at 121.6 nm in a N₂
303 and CO₂ atmosphere. In laboratory experiments designed to simulate Earth's atmosphere
304 at the origin of life, in which the CH₄ mixing ratio was held at 0.1%, and the CO₂
305 mixing ratio was varied from 0 to 0.5% (suggested to include most reasonable estimates
306 for the early Earth; Pavlov et al., 2000), they found principally molecules with mass
307 over charge ratios (m/z) around 39, 41, 43, and 55 indicative of alkane and alkene
308 fragments. The amount of aromatics of 77 and 91 amu decreased with increasing CO₂.
309 The C/O ratio rather than the absolute concentrations of CH₄ and CO₂ was shown to be
310 the factor most correlated with the chemical composition of the products. Aerosol
311 production was seen to be maximum at C/O ratios close to 1, which according to Lowe
312 and Tice (2004) would have occurred at approximately 2.9 Ga. Approximately spherical
313 particles were found in the experiments with average diameters of about 50 nm.
314 Particles of this size, at the estimated photochemical production rates, would have
315 produced an optically thick layer in the UV but a rather thin layer in the visible (Trainer
316 et al., 2006). However, as observed on Titan, and in laboratory experiments employing
317 an electrical discharge source, these particles readily form fractal aggregates of size >
318 100 nm, consistent with observations of the atmosphere of Titan, thereby increasing
319 significantly the visible attenuation with respect to the UV (Trainer et al., 2006).

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321 Given the intensity of the Lyman- α line (121.6 nm) from hydrogen in the Sun at Earth's
322 upper atmosphere and the probable concentrations of CH₄ at these altitudes, Trainer et
323 al. (2006) estimate an aerosol production rate on early Earth of between $1 \times$
324 10^{13} and 1×10^{15} g year⁻¹, which alone is comparable to, or greater than, the estimated
325 delivery of prebiotic organics from hydrothermal vents and comet and meteorite
326 impacts combined. The free energy in UV-C surface light during the Archean available
327 for the production of the fundamental molecules from primordial gases would have
328 been many orders of magnitude greater than that available through the chemical
329 potential available at hydrothermal vents.

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331 By studying the sulfur isotope record, Domagal-Goldman et al. (2008) suggest that a
332 thick organic haze, which blocked UV light in the 170-220 nm range from the
333 photolysis of SO₂ in the lower atmosphere, arose at 3.2 Ga and persisted until 2.7 Ga.
334 Based on these isotope ratios, they suggest that Earth's atmosphere went from a haze-
335 less to thick haze between 3.2 and 2.7 Ga, and then again to a thin haze after 2.7 Ga.
336 The appearance of the haze may be associated with the appearance of methanogens (and
337 anoxygenic photosynthesizers) around 3.2 Ga, which led to a buildup of CH₄, while
338 continent erosion led to a decline in CO₂, and as the ratio of CH₄/CO₂ became close to
339 one, the organic haze became thicker and spread over the upper atmosphere.

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341 A new study (Crowe et al., 2013) suggests that there were appreciable levels of
342 atmospheric oxygen (3×10^{-4} times present levels) about 3 billion years ago, more than
343 600 million years before the Great Oxidation Event and some 300–400 million years
344 earlier than previous indications for Earth surface oxygenation. The researchers suggest
345 that the observed levels are about 100 000 times higher than what can be explained by
346 regular abiotic chemical reactions in Earth's atmosphere and, therefore, the source of
347 this oxygen was almost certainly biological.

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349 There is evidence of oxygenic photosynthesis by at least ~ 2.78 Ga in the presence of 2-
350 α methyl hopanes from O₂-producing cyanobacteria (Brocks et al., 1999) and sterols
351 from O₂-requiring eukaryotes (Summons et al., 1999) in sediments of this age (Brocks
352 et al., 2003). The buildup of oxygen consumed the CH₄ in the atmosphere leading to a
353 reduction in the organic haze. The oxygenation of Earth's atmosphere may have begun
354 in earnest at about 2.9 Ga but accelerated at about 2.45 Ga and would have removed
355 most of the CH₄ greenhouse gas from the atmosphere by about 2.2-2.0 Ga (Rye and
356 Holland, 1998).

357

358 Other lines of geochemical evidence suggest that the major oxygenation event occurred
359 in the atmosphere at about 2.2 Ga, with atmospheric O₂ levels rising sharply from < 1%
360 of present atmospheric levels to about 15% of present atmospheric levels, during a
361 relatively short period from 2.2 to 2.1 Ga (Nisbet and Sleep, 2001; Wiechert, 2002).
362 Studies of carbon deposition rates and the sulfur isotope record suggest another abrupt
363 rise in atmospheric oxygen occurring at about 0.6 Ga, which probably reached present
364 day levels (Canfield and Teske, 1996). Deep ocean environments on the other hand are
365 thought to have remained anoxic and highly sulfidic during the long geological period
366 from 2.2 to 0.6 Ga when atmospheric O₂ was only about 15% of present day levels
367 (Anbar and Knoll, 2002).

368

369 The spawning of wildfires requires an atmospheric oxygen content of at least 13% and
370 the first evidence of charcoal deposits comes from the Silurian at 420 Ma (Scott and
371 Glasspool, 2006). Recent results from the analysis of plant material trapped in amber
372 suggest that oxygen levels did not rise to present day levels of 21% by mass until very
373 recently, remaining at levels of between 10 and 15% from 250 Ma to 30 Ma (Tappert et
374 al., 2013).

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376 Through an analysis of the imprint of "fossil raindrops" from 2.7 Ga discovered in
377 Ventersdorp in the North West Province of South Africa, Som et al. (2012) have
378 concluded that atmospheric pressure in the Archean was probably similar to today's and
379 certainly no more than twice as large as today.

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381 The amount of water in the present day hydrologic cycle, and thus in today's
382 atmosphere, has been predicted to rise by about 3.2% for every 1°K increase in surface
383 temperature due to greenhouse warming (Kleidon and Renner, 2013). Another
384 determination can be made from the saturation pressure of water which increases about
385 6.5% per degree. With temperatures in the Archean at least 50 °C above those of today,
386 a conservative estimate for the amount of water vapor in the atmosphere would be at
387 least twice as large as today.

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389 **3. The organic pigment tree of life**

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391 The evolutionary history of organic pigments is a subject barely considered hitherto but
392 crucial for framing life and evolution within the proposed thermodynamic context.
393 From this thermodynamic perspective, one would expect the history of pigment
394 appearance and evolution to be correlated with the evolution of the solar spectrum at
395 Earth's surface.

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397 It is probable that the evolution of organic pigments would have kept pace with the
398 evolving transparency of Earth's atmosphere and that there should be a continuity over

399 time of solar photon absorption and dissipation, reflecting the Earth's surface solar
400 spectrum, from the earliest molecules of life (nucleotides, amino acids, organic
401 cofactors) to present-day phototropic organisms with their extensive array of pigments.
402 It is proposed here that an important hallmark of the evolution of life on Earth is the
403 proliferation of organic pigments over Earth's surface and their structuring in response
404 to changes of the entropically most intense part of the prevailing surface solar spectrum.
405 This continuous history of pigment proliferation and re-structuring can be resolved into
406 stages, and we chose six basic stages which roughly correlate with particular geological
407 eons supporting particular atmospheric transparencies.

408 409 3.1 World of earliest pigments (Hadean eon, ~ 4.6 – 4.0 Ga)

410 The presence of both liquid and gaseous water phases 4.3 billion to 4.4 billion years ago
411 (Mojzsis et al., 2001) implies the existence of a primitive water cycle with the probable
412 involvement of organic pigments (Michaelian, 2009). It is generally believed that
413 various pre-biotic inorganic and organic substances such as H₂, N₂, HCN, CO₂, CH₄ and
414 polycyclic aromatic hydrocarbons were abundant in this early aquatic environment and
415 that UV light and lightning acting on these molecules could have led to more complex
416 organics (Miller S., 1953; Cleaves et al., 2008). Whether the origin of the prebiotic
417 organic material was predominantly terrestrial or extraterrestrial is irrelevant to the main
418 premise of this paper. Complex organic molecules are, in fact, ubiquitous throughout
419 the cosmos and are formed basically by the action of UV light on simpler prebiotic
420 organic and inorganic carbon compounds (Callahan et al., 2011; Kwok, 2009;
421 Gerakines et al., 2004).

422
423 Many species of organic molecules (especially those with conjugated systems –
424 Zollinger, 2003) when dissolved in water are very efficient absorbers and dissipaters of
425 UV and visible photons and should therefore be considered as organic pigments during
426 the Hadean and Archean eons. Fast internal conversion through a conical intersection in
427 polyatomic molecules is a result of the coupling of the electronic modes to the
428 vibrational modes, in particular through those attributed to the OH- and CH- groups
429 (Vekshin, 2002). The vibrational energy is then dissipated and channeled via
430 intermolecular vibrational energy transfer to nearby hydrogen bonds between water
431 molecules fomenting evaporation.

432
433 These properties would have given them excellent entropy producing capacity, and
434 therefore, it is probably not a coincidence that the fundamental molecules of life
435 (nucleic acids, aromatic amino acids, enzymatic cofactors) are actually organic
436 pigments in the UV-C-UV-B range. These molecules, that are at the foundations of life
437 today, could have floated on the surface of the primordial ocean in monomeric or single
438 strand polymeric form, absorbing and dissipating UV and visible solar photons,
439 transferring this energy to surrounding water molecules and enhancing in this manner
440 the early water cycle and Earth's global entropy production in its solar environment
441 (Michaelian, 2012a).

442
443 In support of this conjecture is the fact that the five naturally occurring nucleic bases
444 (adenine, guanine, thymine, cytosine, uracil) are UV-pigments which absorb in the 240-
445 290 nm UV region, the short wavelength part of the solar spectrum which could have
446 penetrated Earth's early Hadean and Archean atmosphere (Sagan, 1973), dissipating this
447 radiation into heat with subpicosecond singlet excited state lifetimes (Pecourt et al.,
448 2000; Middleton et al., 2009). Another interesting and corroborating fact is that their

449 non-natural tautomers have much longer decay times (Serrano-Andrés and Merchán,
450 2009; Gustavsson et al., 2006; Crespo-Hernández et al., 2004) implying much lower
451 entropy producing efficacy and photochemical stability. Furthermore, it has been
452 demonstrated that the guanine-cytosine Watson-Crick base pairs exhibit superior
453 photon-dissipation characteristics compared to other possible base pairing between
454 these nucleobases (Abo-Riziq et al., 2005). Woutersen and Cristalli (2004) have found
455 that vibrational relaxation of the NH-stretching mode occurs much faster in the adenine-
456 uracil Watson-Crick base pairs compared to isolated monomeric uracil and that the
457 hydrogen bonding between these bases is responsible for the extremely fast vibrational
458 relaxation in the base-pair system. Therefore, the coupling of nucleobase photon
459 dissipation to the water cycle and the resulting increase in entropy production can be
460 seen as the thermodynamic driving force for their polymerization into RNA/DNA and
461 the ensuing replication of these polymers through an ultraviolet and temperature
462 assisted RNA/DNA reproduction (UVTAR; Michaelian, 2009, 2011).

463
464 Other complex issues, like the homochirality of life (right-handedness of the natural
465 RNA and DNA enantiomers and the left-handedness of amino acid enantiomers) and an
466 explanation for the beginnings of information storage within DNA (related to the
467 chemical affinity of aromatic amino acids to particular nucleobase sequences) can also
468 be resolved within the scope of this thermodynamic view (Michaelian, 2011).

469
470 In addition to nucleic acids, various other organic UV-C-UV-B-absorbing pigments
471 could have proliferated on the surface of the Hadean ocean driven to high concentration
472 by their photon dissipation capabilities (Michaelian, 2013). UV-C-UV-B light must
473 have acted as a selective force (Sagan, 1973; Mulkidjanian et al., 2003; Serrano-Andrés
474 and Merchán, 2009), not only for stability, but for photon dissipation characteristics and
475 this was probably the onset of an evolution through a thermodynamic natural selection.
476 Among the contemporary, more universal biological molecules, aromatic amino acids
477 (phenylalanine, tyrosine, tryptophan, histidine), cystine (Pace et al., 1995; Edelhoeh,
478 1967); pteridine (pterin and flavin), pyridine, quinone, porphyrin and corrin cofactors;
479 as well as different isoprenoids (Crouse et al., 1963), all absorb in the UV-C-UV-B,
480 and some of them in the visible as well (see Table 1).

481
482 The organic heterocyclic and aromatic cofactors thiamine, riboflavin, folic acid,
483 nicotinamide, pyridoxine, ubiquinone, phytomenadione, hydroxocobalamin and heme
484 are essential part of the metabolism shared by all three domains of life (Raffaelli, 2011;
485 Caetano-Anollés et al., 2012). Nicotinamide and riboflavin come in the form of
486 nucleotides in coenzymes such as NAD (nicotinamide adenine dinucleotide) and FAD
487 (flavin adenine dinucleotide), and because of their resemblance to DNA/RNA
488 nucleotides (cyclic nitrogenous base attached to pentose-phosphate moiety) they have
489 been proposed as molecular relics from an ancient "RNA world" (White, 1976;
490 Kyrpides and Ouzounis, 1995). The cyclic tetrapyrrole cofactor hydroxocobalamin also
491 contains a nucleotide loop in its structure (5,6-di-methylbenzimidazole ribonucleotide),
492 and because of its involvement in basic metabolic reactions, such as DNA synthesis, it
493 has also been implied as one of the most ancient cofactors (Holliday et al., 2007);
494 which, in our view, might betray the very early association between nucleic acids and
495 tetrapyrroles in the evolutionary history of life.

496
497 Because of their strong absorbances across the UV and visible and proposed early
498 connection with nucleic acids at the time of the origin of life (Kyrpides and Ouzounis,

499 1995) it is conceivable that the pre-cofactor function of these molecules was absorption
500 and dissipation of the available UV and visible solar photons. There is consistency in
501 that they all absorb from 220 nm to 290 nm (except for histidine) and beyond 320 nm
502 but not between 290 and 320 nm as would be expected if the atmospheric aldehydes
503 were absorbing there (Sagan, 1973). Apart from their UV-C-UV-B absorbing
504 characteristics, pterin and flavin coenzymes are known to be photochemically active
505 chromophores in a number of actual photoenzymes and sensory photoreceptor proteins
506 (Kritsky et al., 1997, 2010), suggesting a continuity of function since their first
507 appearance near the origin of life. Examples are pterin- and flavin-based photoreceptor
508 proteins called cryptochromes and phototropins in plants which mediate plant
509 phototropism (Brautigam et al., 2004) and the pigment cyanopterin which functions as
510 UV/blue photoreceptor in cyanobacterial phototaxis (Moon et al., 2010). The cofactor
511 component of these photoreceptor proteins is actually responsible for the absorption of
512 incident visible and UV photons and they have even been proposed as ancient pre-
513 chlorophyll photosynthetic pigments (Kritsky et al., 2013a, 2013b). The amino acid
514 tryptophan has been found to play a similar role of sensing UV-B light in the UVR8
515 plant photoreceptor (Christie et al., 2012).

516
517 Several abiotic syntheses routes for the nucleobases and organic cofactors have been
518 devised using UV light. Powner et al. (2009) have shown the feasibility of
519 ribonucleotide production under plausible prebiotic conditions (bypassing the difficult
520 production of ribose and free pyrimidine nucleobases separately) by employing UV
521 light at 254 nm and a heating and cooling cycle which enhanced ribonucleotide
522 synthesis over other less endergonic products. Bernstein et al. (1999) have obtained
523 quinones from polycyclic aromatic hydrocarbons (PAHs) in water ice which was
524 exposed to ultraviolet radiation under astrophysical conditions. Nicotinamide (Dowler
525 et al., 1970; Cleaves and Miller, 2001), pyridoxal (Austin and Waddell, 1999) and
526 flavin-like compounds (Heinz et al., 1979; Heinz and Ried, 1981; Heinz and Ried,
527 1984) have also been obtained in experiments under prebiotic conditions.

528
529 Pigment-catalyzed evaporation may have led to increased concentration of organics and
530 ions in the sea surface layer thus promoting molecular interactions. In this manner an
531 early association through chemical affinity between the replicating nucleic acids and
532 other pigment molecules is plausible. Yarus et al. (2009) have provided experimental
533 evidence for a stereochemical era during the evolution of the genetic code, relying on
534 chemical interactions between amino acids and the tertiary structures of RNA binding
535 sites. According to their results a majority (approximately 75%) of modern amino acids
536 entered the code during this stereochemical era; nevertheless, only a minority
537 (approximately 21%) of modern codons and anticodons retain clear vestiges of these
538 original RNA binding sites. Interestingly, the binding site for the aromatic amino acid
539 tryptophan is among the simplest of the amino acid binding sites known, as well as
540 selective among hydrophobic side chains, and there is a recurring CCA sequence (a
541 tryptophan anticodon triplet) which apparently forms one side of the binding site
542 (Majerfeld and Yarus, 2005). Moreover, Polyansky and Zagrovic (2013) have provided
543 strong evidence for the stereochemical foundation of the genetic code and suggest that
544 mRNAs and cognate proteins may in general be directly complementary to each other
545 and associate, especially if unstructured. Their results show that of all 20 proteinogenic
546 amino acids, tryptophan has the highest binding affinity for purines, and histidine has
547 the highest binding affinity for pyrimidines, followed by phenylalanine and tyrosine.
548

549 Toulmé et al. (1974) tested the binding of tryptophan-containing small peptides to heat-
550 denatured and UV-irradiated DNA, which resulted in direct stacking interaction
551 between the indole ring of tryptophan and single-stranded regions of DNA, that lead to
552 tryptophan fluorescence quenching, and also a preferential binding of the peptide to
553 thymine dimers which photosensitized the splitting of the dimer, possibly acting as a
554 primordial photolyase enzyme. The quenching of one molecule by another is
555 accomplished through the population of the vibrational levels of the quencher molecule,
556 in much the same way as internal conversion on single molecules (Vekshin, 2002).

557

558 Mayer et al. (1979) have tested oligopeptides containing tyrosyl, lysyl, and alanyl
559 residues which bind to polynucleotides and found that tyrosyl fluorescence of the
560 peptides is quenched in their complexes with both single-stranded and double-stranded
561 nucleic acids. An energy transfer mechanism from tyrosine to nucleic acid bases was
562 proposed to account for fluorescence quenching in oligopeptide complexes with double-
563 stranded DNAs. They further theorize that due to the specificity of its stacking
564 interaction for single-stranded nucleic acid structures, tyrosine might be involved
565 through such interactions in the selective recognition of single strands by proteins.

566

567 These data give clues as to the origin of the genetic code. It is plausible that the initial
568 association of nucleic acids was with small peptides containing aromatic amino acids
569 which bound preferentially to specific DNA/RNA sites, thus forming symbiotic-like
570 systems in which nucleobases provided fluorescence quenching through internal
571 conversion of the excited aromatic amino acid residues, and the peptides provided a
572 larger UV-C-UV-B photon absorption cross section and primitive enzymic functions,
573 like the splitting of thymine dimers. Apart from the increased dissipation of the coupled
574 system, the larger cross section afforded by aromatic amino acids and cofactor
575 molecules would produce more local heating, favoring denaturation of DNA/RNA in an
576 ever colder sea, thus fomenting replication and so maintaining and even incrementing
577 entropy production through photon dissipation (Michaelian, 2009, 2011).

578

579 3.2 World of primitive pigment complexes (early Archean eon, ~ 4.0 - 3.8 Ga)

580

581 The cooling of the ocean throughout the Archean probably became an important
582 selective force along with photon dissipation in organic pigment evolution, which
583 induced further association of the aromatic amino acids and other pigment molecules
584 with DNA or RNA and growth in complexity of these structures. In order for
585 denaturing, replication and resulting proliferation of the UV-absorbing DNA/RNA
586 polymers to persist in ever colder waters, their auxiliary set of light-harvesting antenna
587 pigments (small peptides and cofactor molecules) had to enlarge and grow in
588 complexity by acquiring primitive enzymatic functions. Michaelian (2011) argues how
589 the thermodynamic driving force of maintaining and even increasing entropy production
590 in ever colder seas most probably fomented the appearance of information content on
591 RNA/DNA and the associated need for their reproductive fidelity. Toulmé et al. (1974)
592 have shown how tryptophan-containing peptides might have played an enzymic role in
593 the maintenance of this fidelity by acting as primitive photolyase enzymes. Goldfarb et
594 al. (1951) have estimated that each peptide bond contributes an average of about 2500
595 to 2800 to the molar absorption coefficient of proteins at 250 nm, and this was probably
596 the thermodynamic reason for the prebiotic synthesis of polypeptides and their
597 association with RNA and DNA under high UV-C and UV-B light conditions of the
598 early Archean.

599

600 By this stage, one can imagine the appearance of primitive virus-like vesicles, made of
601 nucleic acid interior (core) and an envelope (shell) made of enzymically-active, but still
602 photon dissipating, proteins and other smaller pigment molecules, with simple
603 metabolic reactions between them and the surrounding dissolved ions and molecules.
604 Biochemist Sidney Walter Fox and co-workers (Fox and Kaoru, 1958) have synthesized
605 protein-like chains dubbed “proteinoids” from a mixture of 18 common amino acids at
606 70°C in the presence of phosphoric acid. When present in certain concentrations in
607 aqueous solutions, proteinoids form small structures called microspheres, protobionts,
608 or protocells. They bear much of the basic features provided by cell membranes.
609 Evreinova et al. (1974) were able to produce stable protein-nucleic acid-carbohydrate
610 coacervate drops stabilized by quinones which also absorb in the UV-C (see Table 1).

611

612 Proteinoid-based protocells enclosing DNA/RNA molecules could have been the first
613 cellular life forms on Earth. The association of these amino acid proteinoid chains
614 around a central RNA or DNA was again thermodynamically driven by the increase in
615 the photon cross section offered by the amino acids taking advantage of the much
616 superior dissipation characteristics of the RNA and DNA molecules, providing sub-pico
617 second de-excitation of these photon excited aromatic amino acids to the ground state
618 through internal conversion.

619

620 3.3 World of pigment-carrying protocells (early Archean eon, ~ 3.8 – 3.5 Ga)

621

622 Ancient (3.2 – 3.6 Ga) sedimentary rocks from the Barberton Greenstone Belt in South
623 Africa and Swaziland and the Pilbara Craton in Western Australia have been found to
624 contain prokaryotic microfossils (Noffke et al., 2013; Schopf, 2006). Evidence in these
625 rocks suggests that 3.5 Ga old prokaryotic microorganisms flourished in the form of
626 microbial mats and stromatolites. Stromatolites represent accretionary sedimentary
627 structures from shallow water environments, produced by the activity of prokaryotic,
628 photoautotrophic microorganisms, living in mucilage-secreting communities known as
629 microbial mats (Schopf, 2006).

630

631 This antiquity of autotrophic (and possibly photosynthetic) activity is further
632 corroborated by chemical markers like the ratio of C^{13}/C^{12} in sedimentary organic
633 carbon (kerogen), which indicates a continuous record of biological CO_2 fixation that
634 goes back 3.5 - 3.8 Ga (Schidlowski, 1988, 2001). Among the earliest evidence for life
635 on Earth is the biogenic graphite discovered in old metasedimentary rocks in Western
636 Greenland dated at about 3.7 Ga (Ohtomo et al., 2014). Studies of isotopes have
637 identified traces of methanogens and methanotrophs, and also of active carbon, nitrogen
638 and sulfur cycles dating back as early as 3.5 Ga, and being very similar to modern
639 cycles already at around 2.7 Ga (Nisbet and Sleep, 2001; Grassineau et al., 2001).

640

641 The last universal common ancestor (LUCA) from which all organisms now living on
642 Earth descend is estimated to have lived some 3.5 to 3.8 billion years ago (Glansdorff et
643 al., 2008; Doolittle, 2000). It had properties currently shared by all three domains of
644 life: cellular structure with water-based cytoplasm, enclosed by a lipid bilayer
645 membrane; genetic code based on DNA or RNA; L-isomers of the 20 proteinogenic
646 amino acids; ATP as an energy intermediate; common enzymes and cofactors, etc.

647

648 Since many more amino acids are chemically possible than the twenty found in modern
649 protein molecules, and many other nucleotides are possible besides A, T, G, C, U,
650 Theobald (2010) put forward the possibility that LUCA was not alone, but only a
651 member of an ancient, diverse microbial community. However, a strong thermodynamic
652 reason, consistent with our proposition, for the existence of only the nominal
653 nucleotides and their Watson-Crick pairing is that these have non-radiative de-excitation
654 times orders of magnitude shorter than any other nucleotides and their possible pairings,
655 even of those energetically more favorable (Abo-Riziq et al., 2005; Woutersen and
656 Cristalli, 2004).

657
658 From the optics of the thermodynamic dissipation theory for the origin and evolution of
659 life (Michaelian, 2009, 2011), and the established facts given above, a picture of life on
660 Earth prior 3.5 Ga can be inferred. From the multitude of different pigment complexes,
661 the one that gave rise to the line of the LUCA evolved to be a prokaryote-like, lipid-
662 membrane vesicle (protocell) where the “old generation” of UV-dissipaters (DNA/RNA
663 plus some proteins) began to take on a new secondary role of information-carriers and
664 chemical catalysts, becoming genetic material, ribosomes and enzymes, with a new
665 function - to execute the synthesis, support, and proliferation of the “new dissipating
666 generation of pigments” more completely covering the evolving solar spectrum
667 available at Earth's surface.

668
669 Cellular structure provided two new fundamental conditions: their increased photon
670 cross section for dissipation, and protection of the progressively more intricate
671 biochemical activity from the outside environment. Because increasing amounts of
672 visible photons were making it to the surface as volcano produced sulfuric acid clouds
673 similar to those on Venus today began to wane, it is probable that a “new generation” of
674 visible light dissipaters on the cell surface, as membrane-bound light-harvesting antenna
675 molecules, became increasingly common. Different types of organic pigments could
676 have filled this role, but limiting our search to the line of the LUCA and keeping in
677 mind the evidence of stromatolites and possible photosynthetic activity by this time,
678 porphyrins/chlorins emerge as an interesting class of candidate pigments.

679
680 Many Urey-Miller-type experiments have readily produced oligopyrroles and
681 porphyrins abiotically using various sources of energy, including electrical discharges
682 (Hodgson and Ponnampuram, 1968; Simionescu et al., 1978), ultraviolet irradiation
683 (Szutka, 1965; Hodgson and Baker, 1967; Meierhenrich et al., 2005), and high
684 temperatures of 70-100°C, compatible with a prebiotic milieu (Lindsey et al., 2009).
685 Porphyrin-like substances have even been found in meteorites (Hodgson and Baker,
686 1964) and Precambrian rocks (Kolesnikov and Egorov, 1977). Porphyrins, in fact, have
687 a chemical affinity to DNA, their chromophore plane intercalates between base pairs of
688 DNA or they form stacked aggregates on its surface (Pasternack et al., 1991; Pasternack
689 et al., 1993; Pasternack and Gibbs, 1996).

690
691 Siggel et al. (1996) have found that amphiphilic porphyrins aggregate in aqueous media
692 and form fibers, ribbons, tubules and sheets. In lateral aggregates, the S_x and S_y
693 components of the monomer Soret band centered around 400 nm are shifted to the blue
694 and red respectively to yield exciton Soret bands at around 350 and 450 nm. There is
695 substantial enhancement of internal conversion and thus quenching of fluorescence in
696 these aggregates as compared to individual porphyrin molecules.

697

698 Chlorophyll (a chlorin derivative, related in structure to porphyrin) is also interesting in
699 this respect. Isolated chlorophylls are susceptible to bleaching (the opening up of the
700 tetrapyrrole ring) particularly at 350 nm where there is significant absorption. However,
701 at high concentration they form aggregates that are particularly rapid quenchers from
702 the UV-C to the UV-A and therefore stable against photoreactions and break-up
703 (Zvezdanovic and Markovic, 2008). These same authors demonstrate that an accessory
704 pigment environment has rather little effect on chlorophyll bleaching independent of the
705 wavelength of the light, and therefore the assignment of accessory pigments as
706 protectors of the photosynthetic system may be misguided. It is more likely that since
707 the Archean, porphyrins, and later "accessory" pigments, formed part of an ever larger
708 dissipative system, performing the most relevant thermodynamic dissipation associated
709 to life, that of converting short wavelength photons into many long wavelength photons.

710
711 Accordingly, primitive protocells could have acquired porphyrin molecules from UV-C
712 and UV-B and visible- dissipating aggregates in the environment, integrating them in
713 the nucleic acid-protein complex as light-harvesting antenna pigments. The primitive
714 cell then likely "learned" very early in its evolution how to synthesize its own
715 endogenous porphyrin, an assumption which can be backed by the transfer-RNA
716 dependent aminolevulinic acid formation during chlorophyll biosynthesis in phototropic
717 organisms, indicating that porphyrin biosynthesis is as ancient as that of proteins
718 (Kumar et al., 1996; Jahn et al., 2006). In support of this view come recent phylogenetic
719 tree reconstructions by Caetano-Anollés et al. (2012), which classify the short-chain
720 dehydrogenase/oxidoreductase superfamily of enzymes (SDR) among the most ancient
721 proteins ever used by cells. Their metabolic activities spread throughout numerous
722 different metabolic subnetworks, of which porphyrin and chlorophyll metabolism has
723 been shown to be the most ancient (Caetano-Anollés et al., 2012).

724
725 Further evidence for the antiquity of porphyrin-type pigments and their role in
726 dissipation processes comes from the work of Mulkidjanian and Junge (1997). On the
727 basis of evidence from sequence alignments between membrane-spanning segments of
728 bacterial and plant proteins involved in photosynthesis (photosynthetic reaction centers
729 and antenna complexes) they have postulated the existence of a large ancestral
730 porphyrin-carrying protein, which they describe as a primordial UV-protector of the
731 cell. UV "protection" functioned in a way that the aromatic amino acid residues of the
732 membrane protein clustered around the porphyrin/chlorin molecule were primary
733 receivers of UV-quanta and transferred this excitation energy to the nearby pigment
734 moiety which underwent fast internal conversion to the lowest singlet state releasing the
735 photon energy in thermal energy.

736
737 Chlorophyll, common in most modern phototropic organisms, plays essentially this
738 dissipative role. It has two excitation levels (the high energy Soret band in the near UV
739 and the low energy Qy band in the red) and a photon absorbed in the Soret band
740 dissipates extremely efficiently to the Qy band before the remaining free energy can be
741 used in photosynthesis. Enhancement and redshift of the Qy band would provide even
742 more efficient photon dissipation and this is indeed a recognizable trait in a proposed
743 evolutionary trajectory from protoporphyrin IX via protochlorophyll *c* to chlorophyll *c*
744 and then to chlorophyll *a* (Olson and Pierson, 1987; Larkum, 1991).

745
746 Mulkidjanian and Junge (1997) further theorize how at the beginning this dissipative
747 photochemical activity in the cell functioned only in the context of UV-"protection", but

748 later mutations, which caused the loss of certain pigment components, led to obtainment
749 of redox cofactors and a gradual transition from purely dissipative to productive
750 photochemistry, i.e. from UV-“protection” to photosynthesis. In the context of the
751 thermodynamic dissipation theory for the origin of life, this putative pigment-carrying
752 membrane protein, instead of being an “ancient UV-protector” is more appropriately
753 designated as the “new generation” of UV-dissipating pigments, continuing, from the
754 nucleic and aromatic amino acids, the thermodynamic role of photon dissipation and
755 catalysis of the water cycle. Since porphyrin/chlorin-carrying proteins are universal to
756 all three domains of life (Georgopapadakou and Scott, 1977; Suo et al., 2007), either as
757 chlorophyll-carrying photosystems, or heme-carrying cytochromes, it is quite plausible
758 that this primordial porphyrin-protein complex was the main dissipating unit of the
759 LUCA protocells.

760
761 Whether UV-based anoxygenic photosynthesis powered these primitive cells or they
762 were dependent on chemoautotrophy, cannot be ascertained although previously
763 mentioned evidence (chemical markers, stromatolites) imply that autotrophy and CO₂
764 fixation (possibly photoautotrophy) was well established by this time. Early emergence
765 of photosynthetic autotrophy is consistent with the thermodynamic dissipation since it
766 would have led to accelerated pigment proliferation and hence still greater photon
767 dissipation (Michaelian, 2009, 2011). Heterotrophs most likely developed somewhat
768 later than autotrophs and were probably more prevalent in deeper waters feeding on the
769 “rain” of organic material from the surface. From a thermodynamic perspective they can
770 be considered as “gardeners” of the autotrophs, playing a crucial role in the constant
771 recycling of the elements needed for pigment synthesis (phosphate, nitrogen, carbon
772 etc.) and in facilitating their expansion into new, initially inhospitable, areas.

773 774 3.4 World of pigment-carrying protocyanobacteria (Archean eon, ~ 3.5 – 2.5 Ga)

775
776 There is a continuity of stromatolites in the fossil record from 3.5 Ga to 2.5 Ga, even
777 though Archean geological units are relatively scarce when compared to those of the
778 Proterozoic (Schopf et al., 2007). The distribution of Archean stromatolites seems to
779 consistently parallel the estimated temporal distribution of Archean sediments that have
780 survived to the present, in a way that most stromatolite fossils have been reported from
781 younger rocks (2.5 – 3.0 Ga) relatively abundant in the fossil record, and fewer from
782 older rocks (3.5 – 3.0 Ga) relatively scarce in the fossil record. Biogenicity of these
783 sediments has been backed by the discovery of microscopic fossils with microbe-like
784 morphologies typical of later, less questionable, Proterozoic microfossils: sinuous
785 tubular or uniseriate filaments, small rod-shaped bodies, or unornamented coccoids
786 (Schopf, 2006). Geochemical evidence from the Buck Reef Chert (250 to 400 meter
787 thick rock running along the South African coast) show that it was most likely produced
788 by the activities of phototrophic microbial communities about 3.4 billion years ago
789 (Tice and Lowe, 2004, 2006). The same authors characterize the inhabitants of these
790 ancient microbial communities as partially filamentous phototrophs which probably
791 used the Calvin–Benson–Bassham cycle for CO₂ fixation according to local carbon
792 isotope composition. Interestingly, they failed to notice any traces of life in the deeper
793 (>200 m) aquatic environments.

794
795 Combining this evidence with the results of Crowe et al. (2013) for the beginnings of
796 atmosphere oxygenation would indicate that the advent of oxygenic photosynthesis was
797 sometime prior 3 Ga, and was carried out by cyanobacteria-like organisms usually

798 referred to in the scientific community as protocyanobacteria (Olson, 2006; Garcia-
799 Pichel, 1998).

800

801 Cyanobacteria are believed to be one of the most ancient groups of organisms on this
802 planet and among the earliest to branch off in a separate phylum (Altermann and
803 Kazmierczak, 2003). As the only prokaryotes which carry out oxygenic photosynthesis,
804 there is little doubt among scientists today that they were responsible for the production
805 and accumulation of oxygen and ozone in the atmosphere (Bekker et al., 2004).

806 Oxygenic photosynthesis is distinguished by the presence of two photosystems
807 (photosystem I and photosystem II) of which photosystem II incorporates the water-
808 splitting complex (four oxidized manganese atoms and a calcium atom, held in place by
809 proteins), and the utilization of water as a reductant, which generates oxygen as a waste
810 product (Kiang et al., 2007; Allen and Martin, 2007). In contrast, anoxygenic types of
811 photosynthesis employ only one of the photosystems (photosystem I or photosystem II),
812 but never both, lack the water-splitting complex and utilize other electron donors:
813 hydrogen, hydrogen sulfide, ferrous ions, nitrite etc. (Kiang et al., 2007; Bryant and
814 Frigaard, 2006).

815

816 Because of the relatively higher complexity of their photosynthetic apparatus when
817 compared to other photosynthetic bacteria (purple bacteria, green sulfur bacteria, green
818 non-sulfur bacteria, heliobacteria) cyanobacteria haven't been traditionally considered
819 as a lineage in which photosynthesis could have developed. But a recent study by
820 Mulkidjanian et al. (2006) and Mulkidjanian and Galperin (2013), comparing genome
821 sequences of photosynthesis-related genes in phototropic members of diverse bacterial
822 lineages, has come to the conclusion that photosynthesis most likely had its origins in
823 the cyanobacterial lineage and only later spread to other bacterial phyla by way of
824 lateral gene transfer. The study also proposes that this direct ancestor of the
825 cyanobacteria – protocyanobacteria, was an anaerobic, mat-dwelling phototroph which
826 probably used hydrogen as a reductant, and inherited its photosynthetic machinery from
827 mutations of the earlier “UV-protective” membrane protein. The invention of the water-
828 splitting complex came later, but not before the lateral gene transfer to other bacteria
829 which lack it, and, according to Mulkidjanian and Junge (1997), this complex was
830 probably formed by the trapping of Mn-atoms in the cavities of earlier porphyrin-
831 binding sites in photosystem II. Manganese ions of the type that occur in the water-
832 splitting complex are readily oxidized by ultraviolet light of wavelengths less than 240
833 nm (Russel and Hall, 2006) and since there was no ozone to filter out the Sun's UV-rays
834 before the origin of water splitting, these excited Mn-atoms probably served as electron
835 donors to protocyanobacteria which were introduced into an ancient, aquatic Mn-
836 containing environment, and only later incorporated them into their photosystem II
837 (Allen and Martin, 2007; Johnson et al., 2013). It is worth mentioning that a Mn-cluster
838 with electron vacancies is able to dissipate the energy of a single UV photon through the
839 formation of hydrogen peroxide from water (Mulkidjanian and Junge, 1997). The
840 reaction of dioxygen production from water catalyzed by four low-energy photons of
841 red light may have gradually developed at a later phase of protocyanobacterial
842 evolution.

843

844 Dissipation of the intense UV-radiation during this geological period could have further
845 been enhanced by the invention of an even greater variety of UV-absorbing compounds
846 like the contemporary UV-A and UV-B absorbing mycosporine-like amino acids and
847 scytonemin (Shick and Dunlap, 2002; Castenholz and Garcia-Pichel, 2002; Ferroni et

848 al., 2010). These pigments, widespread in modern cyanobacteria, algae and other
849 aquatic organisms and usually defined as UV-protectants or sunscreens, are most likely
850 remnants of Archean, protocyanobacterial, UV-dissipating pigments (Garcia-Pichel,
851 1998). Biosynthetically, mycosporine-like amino acids are derived from intermediates
852 of the shikimate pathway for the synthesis of the aromatic amino acids (Shick and
853 Dunlap, 2002; Portwich and Garcia-Pichel, 2003), while scytonemin is derived from
854 tryptophan (Balskus et al., 2011), suggesting a later evolutionary appearance of these
855 pigments compared to that of the aromatic amino acids.

856
857 Besides protocyanobacteria and other members of the domain Bacteria, the Archean
858 seas were most likely also harboring the ancestors of modern domain Archaea (Wang et
859 al., 2007; Woese and Gupta, 1981). If the ancestors of cyanobacteria were already
860 present by 3 Ga, it is probable that the line of the LUCA had already branched into the
861 separate domains Bacteria and Archaea at a much earlier point in time, probably as
862 early as 3.5 Ga, or even earlier. No known member of the Archaea domain carries out
863 photosynthesis, although some members of the class Halobacteria are photoheterotrophs
864 which utilize light energy absorbed by the chromoprotein bacteriorhodopsin to
865 synthesize ATP, and their carbon source is organic (Bryant and Frigaard, 2006).

866
867 Mulkidjanian and Junge (1997) hypothesize that the bacteriorhodopsin-based
868 phototropism in Archaea might have also evolved from a “UV-protecting” precursor
869 function, because it has been shown (Kalisky et al., 1982) that a UV-quantum,
870 channeled from the aromatic amino acid residues of the protein moiety, triggers the *all-*
871 *tans* to 13-*cys* isomerization of the retinal moiety in bacteriorhodopsin, followed by its
872 return into the initial isomeric state by slow thermal relaxation. This bacteriorhodopsin-
873 based photon dissipation in Archaea probably evolved as a complementary to the
874 chlorophyll-based in protocyanobacteria for dissipation of visible wavelengths left
875 unabsorbed by chlorophyll (DasSarma, 2006, 2007).

876
877 3.5 World of pigment-carrying cyanobacteria and algal plastids (Proterozoic eon, ~ 2.5
878 Ga – 542 Ma)

879
880 Free oxygen is toxic to obligate anaerobic organisms and the rising concentrations
881 during the early Proterozoic may have wiped out most of the Earth's anaerobic
882 inhabitants at the time, causing one of the most significant extinction events in Earth's
883 history known as the Oxygen Catastrophe (Sessions et al., 2009; Holland, 2006).
884 Additionally the free oxygen reacted with the atmospheric methane, a greenhouse gas,
885 reducing its concentration and thereby triggering the Huronian glaciation, possibly the
886 most severe and longest snowball Earth episode (Kopp et al., 2005). Despite its toxicity
887 for most anaerobes at the time some lineages successfully adapted “learning” to use it as
888 a terminal electron acceptor in electron transport chains thus heralding the new age of
889 aerobic respiration (Sessions et al., 2009; Raymond and Serge, 2006).

890
891 Biomarker evidence (the presence of long-chain 2-methylhopanes) suggests that during
892 the early Proterozoic (Paleoproterozoic) a phytoplankton population was thriving in the
893 ocean, consisting mainly, or entirely, of cyanobacteria (Summons et al., 1999;
894 Falkowski et al., 2004; Canfield, 2005). Unlike other eubacterial phyla, cyanobacteria
895 exhibit a substantially well-studied fossil record, with the earliest unequivocal
896 cyanobacterial fossils dating back around 2.0 Ga which come from two localities, the
897 Gunflint iron formation and the Belcher Subgroup, both in Canada (Sergeev et al.,

898 2002; Golubic and Lee, 1999; Amard and Bertrand-Sarfati, 1997). Schirrmeister et al.
899 (2013) suggest a concurrence of the onset of the Great Oxidation Event, the origin of
900 cyanobacterial multicellular forms and an increased diversification rate of
901 cyanobacteria.

902
903 The first advanced single-celled eukaryotes and multicellular life roughly coincide with
904 the beginning of the accumulation of free oxygen in the atmosphere (El Albani et al.,
905 2010; Falkowski and Isozaki, 2008; Baudouin-Cornu and Thomas, 2007). Currently
906 there is no consensus regarding the origin of the first eukaryotic cell although numerous
907 scenarios have been proposed including fusions between a bacterial and an archaeal
908 ancestors and sometimes even serial merging events (Poole and Penny, 2007). The
909 endosymbiotic hypothesis for the origin of mitochondria suggests that these organelles
910 descend from an aerobic proteobacterium which survived endocytosis by the primitive
911 eukaryotic cell, and thus became incorporated into its cytoplasm (Latorre et al., 2011;
912 Doolittle, 2000). This symbiotic event is estimated to have happened around 1.7 – 2.0
913 Ga according to protein clock estimates (Feng et al., 1997; Emelyanov, 2001), and it's
914 generally assumed that all the eukaryotic lineages that did not acquire mitochondria
915 went extinct (Martin and Mentel, 2010).

916
917 Chloroplasts most likely came about from another endosymbiotic event involving
918 engulfed cyanobacteria into the primitive mitochondria-bearing eukaryotic cell, which,
919 like the origin of mitochondria, is considered to be a singular event in evolution (Stoebe
920 and Kowallik, 1999; McFadden, 2001). This primary endosymbiotic event was still
921 followed by series of secondary and tertiary endosymbiotic events in which eukaryotic
922 hosts engulfed eukaryotic algae, resulting in the formation of secondary plastids in some
923 algal lineages (Cavalier-Smith, 2000; Delwiche, 1999).

924
925 Chloroplasts are the organelles of plants and algae that harbor biochemical pathways for
926 all pigments or pigment-precursors in the cell, like aromatic amino acids, heme,
927 chlorophyll and isoprenoids (Keeling, 2004). All primary chloroplasts belong to one of
928 three chloroplast lineages - the glaucophyte chloroplast lineage, the rhodophyte (or red
929 algal) lineage, and the chloroplastidan (or green algal) lineage (Ball et al., 2011). The
930 second two are the largest, and the green chloroplast lineage is the one that contains
931 land plants (Keeling, 2004). Glaucophyte chloroplasts contain photosynthetic pigments
932 chlorophyll *a*, phycobilins, and phycobilisomes, small antenna-like structures organized
933 on the outer face of thylakoid membranes that are also found in cyanobacteria (Keeling,
934 2004). Red algal chloroplasts contain chlorophyll *a*, phycobilins, and phycobilisomes,
935 where the phycobiliprotein phycoerythrin is responsible for giving many red algae their
936 distinctive red color. Green algal chloroplasts differ from glaucophyte and red algal
937 chloroplasts in that they have lost their phycobilisomes, and contain chlorophyll *b*
938 instead (Kim and Archibald, 2009). Phylogenetic analyses, however, show that the
939 common ancestor of cyanobacteria and chloroplasts had both chlorophyll *b* and
940 phycobilins (Tomitani et al., 1999). The antiquity of chlorophyll *b* and its early presence
941 in the protocyanobacterial lineage might be backed by the fact that it has an absorption
942 peak in the UV-C at around 258 nm (Zalar et al., 2007).

943
944 Shales of the early Mesoproterozoic Roper Group in northern Australia have been found
945 to contain 1.5 Ga old organic fossils called acritarchs which are suspected to be
946 unicellular eukaryotes and most probably algae by virtue of preserved cell wall and
947 cytoskeletal structures (Javaux et al., 2001). Already by 1.2 Ga very modern-looking

948 and well-preserved fossils of red algae start appearing in the fossil record (Butterfield,
949 2000), although more recent work proposes the existence of even older fossils of
950 filamentous algae dating back as far as 1.6 to 1.7 Ga (Bengtson et al., 2009).

951
952 The end of the Proterozoic saw several, relatively short-lived, glaciations, after which
953 multicellular eukaryotic life boomed in the oceans (Ediacara biota) paving the way for
954 the still greater boom during the Cambrian Explosion (Stanley, 2008).

955
956 Atmospheric changes during this eon led to the gradual dimming of UV-C light
957 available at the surface whose dissipation was being relegated from UV-C absorbing
958 biological pigments to biologically-produced stratospheric ozone. The reduced intensity
959 of UV-C intercepted by the biosphere probably induced significant metabolic and
960 pigment-related changes in the biological world. It is therefore conceivable that this was
961 the period of diversification and proliferation of visible-absorbing pigments in
962 cyanobacteria and their chloroplast counterparts in algae. Inside the photosynthetic
963 apparatus, the work of primary photon receivers probably shifted from the aromatic
964 amino acid residues of the light-harvesting antenna proteins (UV-absorbers) to the
965 (bacterio)chlorophyll pigments (visible and near-infrared absorbers). Contemporary
966 carotenoid and phycobilin pigments, which function as accessory pigments to
967 (bacterio)chlorophylls in photosynthesis, absorbing parts of the visible spectrum left
968 unabsorbed by (bacterio)chlorophylls (Rowan, 1989; Nobel, 2009), probably became
969 prevalent during this geological period.

970
971 Carotenoids (divided into carotenes and xanthophylls) are tetraterpenes (contain 8
972 isoprene units i.e. 40 carbon atoms) and because of the multiple conjugated double
973 bonds in their polyene hydrocarbon chain, unlike UV-absorbing isoprene and related
974 isoprenoids with less conjugated double bonds, their absorption maxima shifts to longer
975 wavelengths in the blue-green (Rowan, 1989; Nobel, 2009). Phytoene, a 40-carbon
976 intermediate in the biosynthesis of carotenoids, whose synthesis from two molecules of
977 geranylgeranyl pyrophosphate (GGPP) marks the first committed step in the
978 biosynthesis of carotenoids, has an UV-Vis absorption spectrum typical for a triply
979 conjugated system with its main absorption maximum in the UV-B range at 285 nm
980 (Crouse et al., 1963). Phytofluene, the second product of carotenoid biosynthesis
981 formed from phytoene in a desaturation reaction leading to the formation of five
982 conjugated double bonds, has an absorption spectra in the UV-A range, with maximal
983 absorption at 348 nm (Crouse et al., 1963).

984
985 Phycobilins are linear tetrapyrroles, which could have evolved through the opening of
986 the porphyrin macrocycle, as happens during their biosynthetic pathway from heme
987 (Beale, 1993; Brown et al., 1990). The light-harvesting antennas of cyanobacteria and
988 the chloroplasts of red algae, glaucophytes and some cryptomonads consist of water-
989 soluble protein-phycobilin complexes, known as phycobiliproteins (not present in
990 green algae and higher plants) which efficiently absorb red, orange, yellow, and green
991 wavelengths, not well absorbed by (bacterio)chlorophylls (Rowan, 1989; Nobel, 2009).
992 Ajlani and Vernotte (1998) have shown that phycobiliproteins are not essential for the
993 survival of cyanobacteria by constructing a viable mutant of the cyanobacterium
994 *Synechocystis* PCC 6803 which lacked major photosystem II phycobilin antenna. This
995 phenomenon, seemingly inconsistent with the Darwinian model of evolution, which
996 suggests that organisms do not retain processes unbeneficial for their survival, finds

997 consistency in the thermodynamic dissipation explanation of life if phycobiliproteins
998 are seen more as dissipative structures rather than photosynthetic ones.
999

1000 In addition to phycobilin- and chlorophyll-containing light-harvesting systems,
1001 cyanobacteria possess small chlorophyll-binding polypeptides, dubbed high-light-
1002 inducible polypeptides (HLIPs), which are not involved in photosynthesis and simply
1003 accumulate in the cell in response to intense light exposure and dissipate this energy to
1004 heat (Havaux et al., 2003; Montane and Kloppstech, 2000). This behavior has led
1005 biologists to ascribe a photoprotective role to this class of pigmented polypeptides,
1006 although we believe that their function might be more accurately described from the
1007 thermodynamic viewpoint as dissipaters of light and catalysts of the hydrologic cycle.
1008

1009 3.6 World of pigment-carrying cyanobacteria, algal and plant plastids (Phanerozoic eon,
1010 ~ 542 Ma - present)
1011

1012 The relatively rapid emergence and diversification of many new phyla and species of
1013 animals during the Cambrian period (542 – 488 Ma) is known as the Cambrian
1014 explosion or Cambrian radiation (Erwin and Valentine, 2013; Knoll and Carroll, 1999).
1015 Land plants evolved from chlorophyte algae living in shallow fresh waters, perhaps as
1016 early as 510 million years ago (Raven and Edwards, 2001). The oldest unequivocal
1017 fossils of land plants and fungi date from the late Cambrian period, around 480-460 Ma,
1018 but molecular evidence suggests that they may have colonized the land much earlier,
1019 630 million years ago, even before the Cambrian Explosion and Snowball Earth events
1020 (Clarke et al., 2011, Heckman et al., 2001). The spread of the organic pigments carried
1021 by them to land and their fomentation of a terrestrial water cycle extending ever more
1022 inland, provided the potential for another 30% of Earth's surface area to be cultivated
1023 for photon dissipation.
1024

1025 The chloroplasts of land plants contain the visible-absorbing pigments: chlorophyll *a*
1026 and *b*, different carotenes and xanthophylls, collectively known as photosynthetic
1027 pigments (Ruban, 2012); and the visible- and UV-absorbing flavonoids, which are
1028 phenolic secondary plant metabolites that do not participate in photosynthesis and are
1029 traditionally given UV-protective and antioxidant roles (Gould and Lister, 2006; Agati
1030 et al., 2007). Anthocyanins are flavonoid, water-soluble, vacuolar pigments,
1031 biosynthetically derived from phenylalanine, which occur in all tissues of higher plants,
1032 including leaves, stems, roots, flowers, and fruits. They absorb mainly in the green part
1033 of the spectrum, where chlorophylls and carotenoids do not absorb strongly, and may
1034 appear red, purple, or blue depending on the vacuolar pH (Hatier and Gould, 2009).
1035 Betalains are a class of red and yellow pigments derived from tyrosine, found only in
1036 plants of the order Caryophyllales, where they replace anthocyanin pigments (Stafford,
1037 1994).
1038

1039 Wang et al. (2007) have shown that transpiration rather than photosynthesis is the
1040 process maximized in plants. Transpiration is by far the largest water flux from Earth's
1041 continents, representing 80 to 90% of terrestrial evapotranspiration (Jasechko et al.,
1042 2013). On the basis of analysis of a global data set of large lakes and rivers, Jasechko et
1043 al. conclude that transpiration recycles $62,000 \pm 8,000 \text{ km}^3$ of water per year to the
1044 atmosphere, using half of all solar free energy available on the land surface. Being the
1045 energetically most consuming process in plants one can assume that most photons
1046 absorbed by plant pigments are being dissipated (mainly through the process of non-

1047 photochemical chlorophyll fluorescence quenching (NPQ) - Müller et al., 2001) and
1048 transferred to the breaking of hydrogen bonds between water molecules, which then
1049 evaporate through the stomata of leaves. In this fashion, terrestrial plants play the same
1050 role as phytoplankton (cyanobacteria, diatoms, dinoflagellates) over bodies of water
1051 (Michaelian, 2011, 2012a), and their evolution and colonization of land can be
1052 interpreted as the extension of entropy production through photon dissipation and the
1053 fomentation of the hydrologic cycle over land surfaces. As we have emphasized in this
1054 paper, the same thermodynamic function was performed by the earliest organic
1055 pigments floating on the surface of the primordial Hadean ocean.

1056
1057 The timing of the earliest animal colonization of land surfaces is not precisely known:
1058 there are trace fossils of non-marine, possibly amphibious, arthropods on land around
1059 450 Ma (Johnson et al., 1994; Pisani et al., 2004), but there is also unconfirmed
1060 evidence of older arthropod traces on land around 530 Ma (MacNaughton et al., 2002).

1061
1062 The influence of insects, crustaceans and larger animals in spreading nutrients for the
1063 production of pigments, and thus photon dissipation and the water cycle, over barren
1064 land or mid ocean areas cannot be over emphasized (Michaelian, 2011). Doughty et al.
1065 (2013) have shown how the Pleistocene Amazonian megafauna extinctions dramatically
1066 decreased the lateral flux of nutrients (particularly of phosphate) in all continents
1067 outside of Africa. Lavery et al. (2010) have determined that blue whales feces
1068 contribute enormously to the distribution of iron in the Southern Ocean for the
1069 proliferation of cyanobacteria and thus the sequestering of atmospheric carbon at mid
1070 ocean environments, a contemporary preoccupation but of secondary importance to
1071 photon dissipation.

1072 1073 **4. The organic pigment tree of life correlates with the evolution of the solar** 1074 **spectrum at Earth's surface**

1075
1076 Considering the abiotic and biotic events affecting Earth's atmosphere presented in Sect.
1077 2, and assuming a black-body spectrum for the Sun in the relevant wavelength region, a
1078 coarse grained history of the solar spectrum at Earth's surface can be derived. The
1079 calculations presented below assume a present day black-body solar photosphere at an
1080 effective temperature of 5840 K with an H⁺ stellar atmosphere absorption line centered
1081 on 500 nm, and includes the time dependence of the increase in the solar radius and
1082 increase in surface temperature as considered in Sect. 2.1. The results of the calculation
1083 are presented below and in Figs. 2 and 3.

1084
1085 Before the origin of life at 3.85 Ga and until about 3.2 Ga, the solar spectrum on Earth
1086 included a unique region of between approximately 230 nm and 290 nm of an integrated
1087 flux of $5.5 \pm 2 \text{ Wm}^{-2}$ midday at the equator with the spectral distribution in this UV-C
1088 region peaking at around 260 nm, bounded on the short wavelength side by H₂S
1089 absorption and on the long wavelength side by formaldehyde and acetaldehyde (both
1090 photochemical reaction products of UV light on hydrogen sulfide). From 290 nm to
1091 about 320 nm, little light would have been available on the surface due to absorption of
1092 the aldehydes. Beyond 320 nm up to 700 nm, where the water absorption becomes
1093 important (a warmer Earth would have supported a more humid atmosphere), the
1094 spectrum at Earth's surface in the Archean was probably very similar to the present day
1095 spectrum but of about 30% lower luminosity due to a faint young Sun, providing an
1096 integrated energy flux of approximately 327 Wm^{-2} integrated over 320 to 700 nm

1097 midday at the equator. The biological world in this era consisted of the dominance of
1098 UV-C and UV-B-dissipating pigments in protocells, among them LUCA, and included
1099 the split of the line of the LUCA into Bacteria and Archaea and the early branching of
1100 the protocyanobacterial line within Bacteria.

1101
1102 From 3.2 Ga to 2.7 Ga, a thick upper atmosphere organic haze probably existed due to
1103 the rise of the methanogens, bringing the CH₄/CO₂ ratio close to one, which is the
1104 condition for haze production (Lowe and Tice, 2004). The wavelength dependence of
1105 the resulting albedo would depend on the size of the agglomerates formed in the
1106 atmosphere, probably increasing that of longer wavelengths by a relatively greater
1107 amount (as on Titan today; McGrath et al., 1998), but would have generally increased
1108 the albedo at all wavelengths with an ensuing cooling of Earth's surface locally to
1109 glacier temperatures. The biosphere saw the branching of oxygenic cyanobacteria
1110 within the protocyanobacterial line and the beginning of gradual O₂ accumulation with
1111 the continuing dominance of UV-dissipating pigments but the visible pigments rising in
1112 importance.

1113
1114 From about 2.7 to 2.45 Ga the organic haze produced by UV-C light on CH₄ in the
1115 upper atmosphere began to decline as erosion of the continents and tectonic recycling of
1116 CO₂ reduced the CH₄/CO₂ ratio, thereby increasing the intensity of the spectrum at
1117 Earth's surface between 320 and 700 nm while at the same time ozone, resulting from
1118 oxygenic photosynthesis, was beginning to reduce the intensity of the UV spectrum
1119 between 230 to 290 nm. Dissipation in this wavelength range was now becoming ever
1120 more relegated to life derived ozone in the upper atmosphere. The biosphere was seeing
1121 the diversification of cyanobacteria and the appearance of multicellular forms of
1122 cyanobacteria, increasingly dissipating in the visible.

1123
1124 After about 2.45-2.2 Ga ozone from oxygenic photosynthesis would have reduced light
1125 within the 230-290 nm wavelength range to less than perhaps a few percent of its value
1126 at the beginnings of life ($5.5 \pm 2 \text{ Wm}^{-2}$ at 3.85 Ga). The biosphere was experiencing the
1127 endosymbiosis of mitochondria and chloroplasts and the emergence of eukaryotes.
1128 Visible-dissipating pigments probably became dominant in this era.

1129
1130 The calculation of the evolution of the solar spectrum at Earth's surface is depicted in
1131 Figs. 2 and 3 where at 3.85 Ga we have included the absorption of H₂S and aldehydes,
1132 Rayleigh scattering for atmospheric pressures at an estimated 1.5 times present day
1133 values, and water at roughly twice its average concentration of present day values of 5
1134 mm of precipitable water (Gates, 1980).

1135
1136 The calculated spectrum at 2.9 Ga includes absorption of H₂S and aldehydes, Rayleigh
1137 scattering for atmospheric pressures at about 1.2 times present day values, and water at
1138 roughly 1.5 its average present concentration, plus wavelength independent scattering
1139 due to organic haze increasing the albedo to 0.6.

1140
1141 At 2.2 Ga we include absorption due to oxygen at 0.15 of its present day mass
1142 concentration of 21%, giving an absolute value of 3.2%, and ozone also at 0.15 of
1143 present day concentrations, Rayleigh scattering for atmospheric pressure at 1.2 present
1144 day values, water at 1.2 of its average present day concentration, and scattering due to
1145 organic haze at about 10% of its late Archean concentration.

1146

1147 For the spectrum calculation at present day, 0.0 Ga, we include absorption of oxygen at
1148 21%, ozone absorption and Rayleigh scattering at present atmospheric pressures giving
1149 an integrated energy flow of 865 Wm^{-2} midday at the equator, consistent with measured
1150 values (Gates, 1980).

1151
1152 The calculations presented in Figs. 2 and 3 have internal consistency with; an increase
1153 of about 27% in the integrated energy flow arriving at the top of Earth's atmosphere
1154 since the beginnings of life; a total of 865 Wm^{-2} arriving at Earth's surface with 9% of
1155 the energy flow in the ultraviolet below 400 nm today. Results for the beginning of life
1156 (~3.85 Ga) are 5.5 Wm^{-2} within the 230-290 nm region arriving at Earth's surface and
1157 4.3 Wm^{-2} within the reduced wavelength 240-270 nm region, roughly consistent with
1158 Sagan's (1973) calculation of 3.3 Wm^{-2} .

1159
1160 Figure 3 plots the chromophoric fundamental molecules of life (first organic pigments)
1161 which are common to all three domains of life (see Table 1) at their absorption maxima.
1162 All pigments absorb and dissipate strongly in the 230-290 nm range, just where a
1163 window existed in Earth's Archean atmosphere. The wavelength range of absorption for
1164 each pigment is in fact much wider than can be depicted in the figure, and the
1165 asymmetry around peak absorption in most cases is also substantial. For example,
1166 guanine actually absorbs strongly over the 240-280 nm region but has peak absorption
1167 at 272.75 nm.

1168
1169 The correlation between the absorption spectra of the chromophoric fundamental
1170 molecules of life and the solar spectrum at Earth's surface during the Archean observed
1171 in Fig. 3 is very supportive of our conjecture that these molecules are among the earliest
1172 pigments that arose and evolved dissipating the solar spectrum available at Earth's
1173 surface. It also lends support to the thermodynamic dissipation theory of the origin of
1174 life (Michaelian, 2009, 2011) which suggests that life arose and evolved because it
1175 dissipated the prevailing solar photon flux and would have begun by forming pigments
1176 at the shorter wavelengths, not only because these are the most photochemically active
1177 wavelengths, but because this is the region of greatest possible entropy production per
1178 unit photon dissipated, or per unit energy, upon conversion to a black-body spectrum at
1179 the temperature of Earth's surface.

1180
1181 In Fig. 4 we provide a timeline showing the correlation between the prevailing surface
1182 solar spectrum and the appearance and dispersal of organic pigments.

1183 1184 **5. Discussion and Conclusions**

1185 Given the current understanding of the evolution of solar like stars and a likely, but less
1186 certain, evolution of Earth's atmosphere, we have determined the probable history of the
1187 solar spectrum at Earth's surface. The most notable feature of this analysis is the
1188 existence, since before the beginnings of life at 3.85 Ga until at least 2.7 Ga, of a region
1189 of UV light between 230 and 290 nm of $5.5 \pm 2 \text{ Wm}^{-2}$ integrated flux. There is some
1190 direct empirical evidence for this UV atmospheric window in the form of ^{33}S isotope
1191 inclusions in diamonds dated at 2.9 Ga that could only have been formed through
1192 specific atmospheric photochemical reactions with ultraviolet light in this wavelength
1193 range (Farquhar et al., 2001). This light could have provided the free energy for a
1194 number of photochemical reactions leading to complex organic pigments which are
1195 known today as the "fundamental molecules of life", including RNA, DNA, aromatic
1196 amino acids, organic cofactors, quinones and porphyrins.

1197

1198 These fundamental biomolecules, common to all three domains of life, absorb and
1199 dissipate strongly within the UV-C and the higher energy part of the UV-B range, from
1200 230 to 290 nm, especially when intercalated or coupled externally to RNA and DNA
1201 which could have acted as rapid quencher molecules. A non-linear, non-equilibrium
1202 thermodynamic directive suggests a spontaneous proliferation of these dissipating
1203 molecules, to concentrations much greater than their expected near equilibrium
1204 concentration, over the entire surface of the Earth exposed to this radiation. The
1205 proliferation of these molecules to high concentrations and their global dispersion can
1206 be explained by the fact that the photochemical production of these pigments is an
1207 autocatalytic reaction process established to dissipate the solar photon potential
1208 (Michaelian, 2013).

1209

1210 The proliferation and evolution of these pigment molecules over time, which succinctly
1211 characterizes all biological and even coupled biotic-abiotic evolution (Michaelian,
1212 2012b), can best be described through five basic tendencies; to increase the ratio of their
1213 effective photon absorption cross sections to their physical size, to decrease their
1214 electronic excited state life times, to quench radiative de-excitation channels (e.g.
1215 fluorescence), to cover ever more completely the prevailing solar spectrum, and finally
1216 to disperse over an ever greater surface area of Earth. The appearance of mobile protists
1217 and animals can be seen as fomenting this thermodynamic directive by providing the
1218 vehicle of dispersion and recycling of nutrients with the overall objective of increasing
1219 pigment dispersion and thus the global entropy production of Earth in its solar
1220 environment.

1221

1222 These fundamental molecules today, having lost their direct dissipating utility, have
1223 taken on new roles and are now produced only through complex enzymes and
1224 biosynthetic reaction pathways; however, they are still completely relevant in their
1225 supportive role that they play in fomenting the proliferation and dispersion over Earth's
1226 surface of the contemporary dissipating pigments in the visible and near UV.

1227

1228 The evidence presented here supports the thermodynamic dissipation theory of the
1229 origin of life (Michaelian, 2009, 2011) which states that life arose and proliferated to
1230 carry out the thermodynamic function of dissipating the entropically most important
1231 part of the solar spectrum (the shortest wavelength photons) prevailing at Earth's surface
1232 and that this irreversible process began to evolve and couple with other irreversible
1233 abiotic processes, such as the water cycle, to become more efficient, to cover ever more
1234 completely the electromagnetic spectrum, and to cover ever more of Earth's surface.
1235 This dissipation continues today as the most important thermodynamic function
1236 performed by living organisms as part of a greater dissipating system known as "the
1237 biosphere" (Michaelian, 2012b).

1238

1239 The revelation of strong and complex interactions of living organisms with their
1240 physical environment discovered by Lovelock and collaborators while working on the
1241 Gaia theory (Lovelock, 2005) led them to suggest that the entire Earth was one great
1242 living organism capable of the auto-regulation of its physical attributes such as; the
1243 global temperature, the amount of salinity in the oceans and the oxygen content of the
1244 atmosphere, among other characteristics. This auto-regulation was claimed to occur in
1245 order to increase the suitability of the Earth environment for life. Although during the
1246 early years of Gaia (the 1970's) the theory was unfairly discredited by neo-Darwinists

1247 who insisted on defending the deficient Darwinian paradigm and who maintained a very
1248 narrow view of the nature of life (see for example Richard Dawkins critique of Gaia in
1249 his book "The Selfish Gene" (Dawkins, 1975) and Lovelock's response in "Gaia:
1250 Medicine for an ailing planet" (Lovelock, 2005)) it is now generally accepted that
1251 although Lovelock's Gaia may be more metaphoric than originally conceived, there is
1252 no question that the strong interaction between the biotic and the abiotic, as exposed in
1253 the theory of Gaia, is an accurate description of Nature.

1254
1255 This strong interaction between the biotic and abiotic is exactly what is expected from a
1256 thermodynamic perspective and we would simply call it a "coupling of irreversible
1257 processes". Onsager (1931) showed that this would happen as long as the entropy
1258 production of the coupled system increases as a result. There are many mundane
1259 examples of this type of coupling in the non-equilibrium thermodynamic literature such
1260 as, for example, the Seebeck effect in which an electrical current couples to a heat flow.
1261 We have maintained that photon dissipation in the pigments which are surrounded by
1262 water inside a leaf (or cyanobacteria) couples strongly to the water cycle (Michaelian,
1263 2012a). Together, the system as a whole, pigments in plants plus water cycle, is much
1264 more efficient at dissipating the solar photon flux. The one great "living" organism of
1265 Gaia could therefore be identified with the great non-equilibrium dissipative structure,
1266 involving the coupling of both biotic and abiotic processes, known as the biosphere. The
1267 biosphere is "living" off solar photon dissipation, as Boltzmann first understood many
1268 years ago.

1269
1270 However, and this is where our view differs from that of Gaia, it is entropy production
1271 through photon dissipation which is the *prima causa* of Nature, not life. Although life
1272 may be locally stabilized through the positive feedbacks delineated in Gaia theory, if
1273 other largely abiotic processes are competitive at producing dissipation, given the
1274 prevailing physical conditions at Earth's surface and atmosphere, then Nature will
1275 forsake life, or a great portion of life, for these other processes. This seems to have
1276 occurred during global glaciations (snowball Earth events) where pigments and life
1277 became severely limited geographically. During these global glaciations photon
1278 dissipation seems to have been relegated to shorter wavelengths (where ice absorbs
1279 rather strongly) through sublimation instead of the water cycle, and to photon scattering
1280 at longer visible wavelengths, which also produces entropy (see Michaelian (2012a) for
1281 the cloud case of Venus as an example). This predominantly abiotic dissipation, perhaps
1282 involving pigments (e.g. those discovered in the atmosphere of Venus), to perform the
1283 initial photon dissipation, coupled to an "abiotic" irreversible process (e.g. the giant
1284 southern vortex on Venus), is apparently what seems to be occurring today on the rest
1285 of the planets in our solar system. This parallels very closely the irreversible coupling
1286 on Earth of organic pigment dissipation with the water cycle.

1287
1288 Lotka (1922) saw the evolution of the biosphere in the opportunity for the origin of a
1289 new species which could latch on to a new channel of free energy, the available energy
1290 for which all life competes, and that this would therefore allow ecosystems to grow and
1291 become more adequate for sustaining life. One could say that this observation was, in
1292 some way, an "energetic" precursor to the theory of Gaia in which organisms co-evolve
1293 together and with their abiotic environment to increase the suitability of Earth for
1294 themselves and all life in general. Our suggestion presented here is that these new
1295 channels for latching on to free energy most often become available through the
1296 evolution of new, more efficient, organic pigments which cover, over evolutionary time,

1297 ever more completely the solar spectrum, as well as the evolution of their associated
1298 organismic vehicles which allow the pigments to spread into inhospitable regions of
1299 Earth's surface. This happens, not for making Earth more suitable to life, but for the
1300 greater thermodynamic role of increasing the solar photon dissipation rate of the
1301 biosphere.

1302
1303 In our view, there can be no inherent "interest" in self preservation assigned to life, but
1304 rather it must be viewed as a dissipative structure (process) which surges and wanes in
1305 response to the impressed solar photon potential and to secondary impressed chemical
1306 potentials derived from it. Other, what are traditionally considered as being more
1307 abiotic, routes to this entropy production are also available (such as Earth's water cycle
1308 or the giant southern vortex on Venus) and which route, or coupling of routes, Nature
1309 takes will depend strongly on initial conditions and subsequent perturbation, but will be
1310 guided by the principle (probabilistic) of increasing the global entropy production of
1311 Earth in its solar environment (Michaelian, 2012a).

1312
1313 Our conjecture provides a new avenue for exploration of Earth's ancient atmosphere
1314 based on pigment history analysis. For example, the lack of primordial pigments
1315 absorbing between 290 and 320 nm strongly suggest the presence of aldehydes in the
1316 Archean atmosphere as postulated by Sagan (1973). Finally, our conjecture sheds new
1317 light on the origin of photosynthesis. The demonstrated abiotic production of porphyrins
1318 using UV light and their UV-C and UV-B absorption and dissipation characteristics
1319 when stacked as aggregates and intercalated or coupled externally to RNA or DNA,
1320 suggests that photosynthesis arose as an adjunct to the porphyrins UV light-harvesting
1321 and dissipation function, as postulated by Mulkidjanian and Junge (1997), when the
1322 photochemically active light at Earth's surface began to wane as life produced ozone
1323 took on the dissipative role at these wavelengths in the upper atmosphere.
1324 Photosynthetic proliferation at visible wavelengths then superseded UV-C dissipative
1325 autocatalytic proliferation. A greater in depth analysis remains to be performed on the
1326 relation between RNA/DNA and many of the fundamental pigment molecules of life,
1327 including the amino acids and the porphyrins, and on the relation between dissipation
1328 and photosynthesis. We are presently engaged in analysis and experiments to explore
1329 this line of reasoning.

1330

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1336

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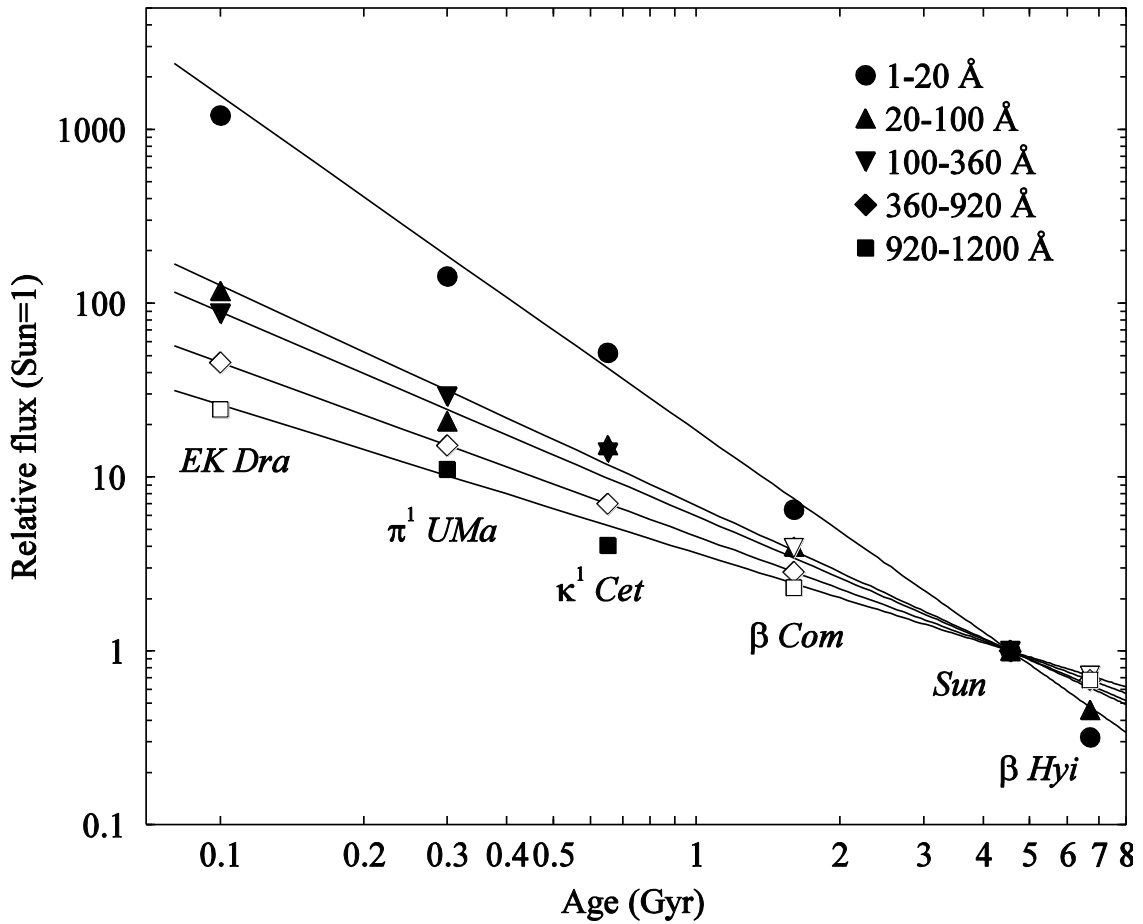
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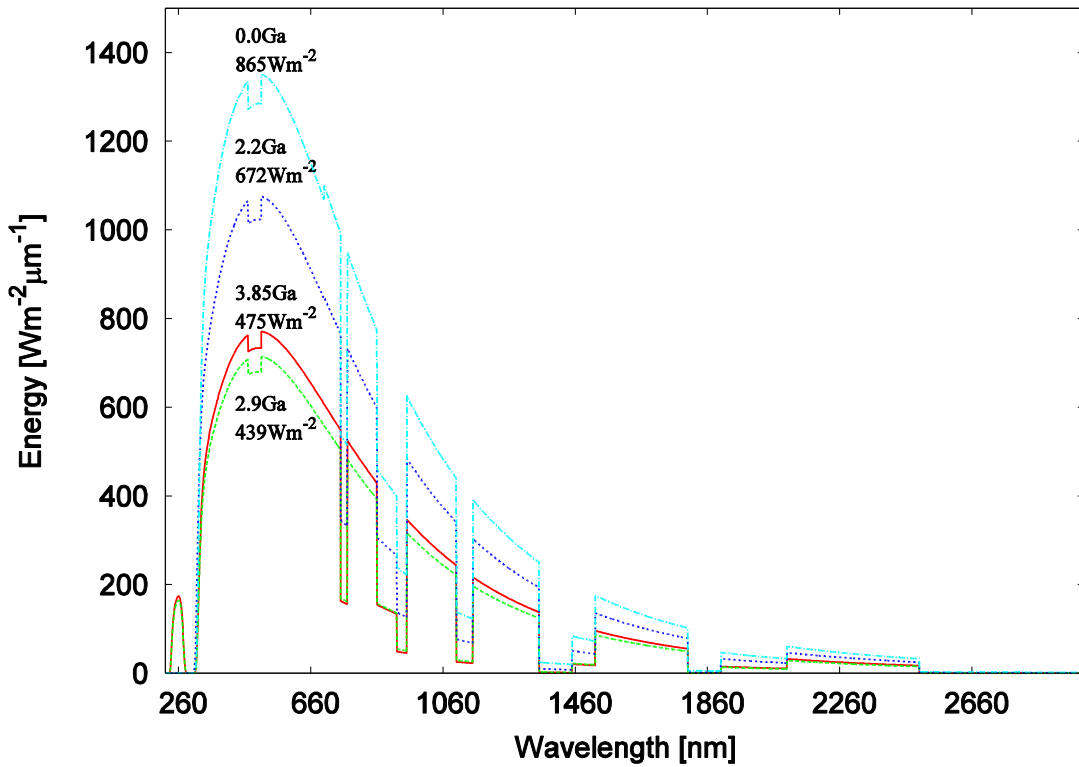
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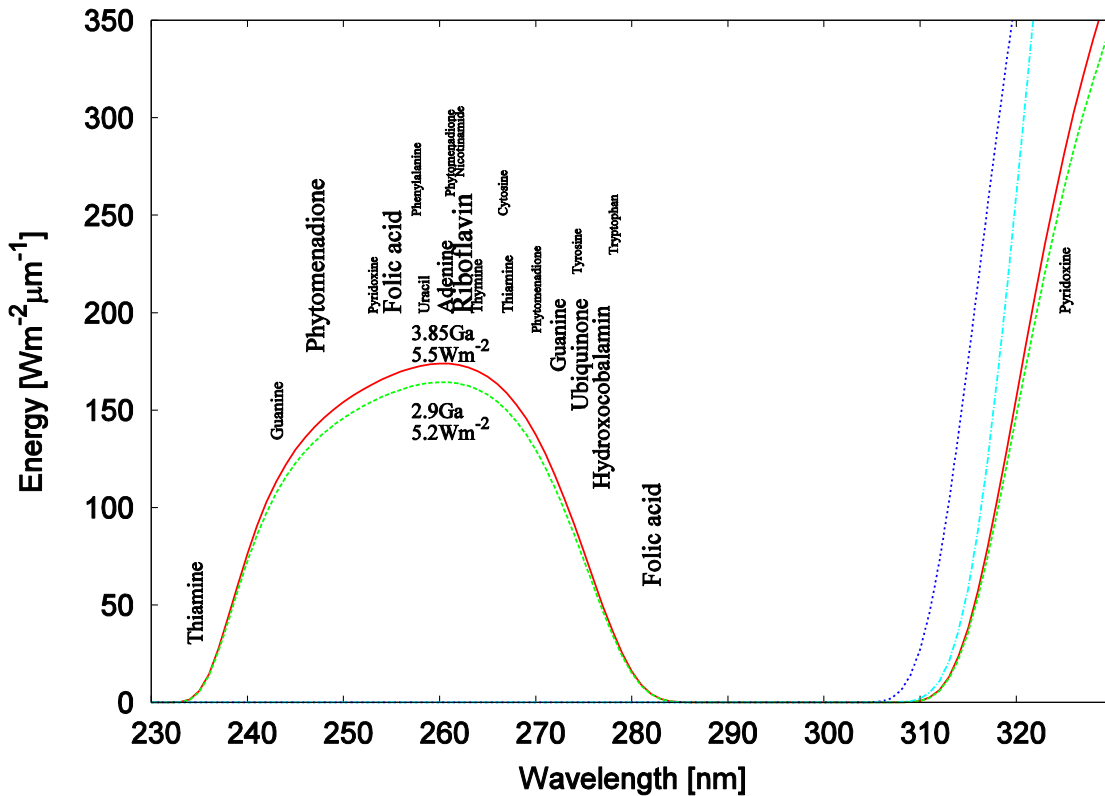
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Figure 1. Solar-normalized fluxes (with respect to those of today) vs. stellar age for different wavelength bands for solar-type stars. Taken from Ribas et al. (2005).

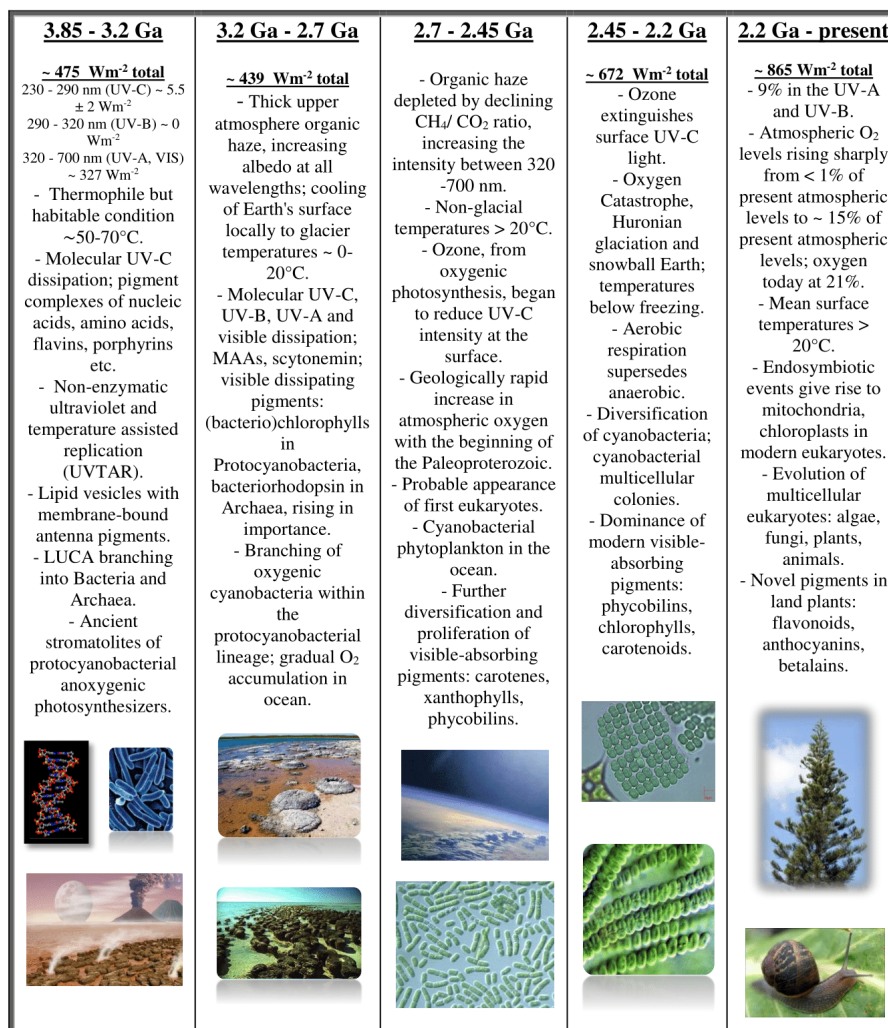


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2213 Figure 2. Calculated solar spectra at Earth's surface at particular dates since present
 2214 assuming the standard solar evolutionary model and using the best available data for the
 2215 atmospheric gasses, their densities, and surface temperature. The total integrated (over
 2216 all wavelengths) energy flows midday at the equator is given below the dates.
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2219
 2220 Figure 3. The wavelengths of maximum absorption of many of the fundamental
 2221 molecules of life (common to all three domains) coincide with the predicted solar
 2222 spectrum at Earth's surface in the UV-C at the time of the origin of life at 3.85 Ga and
 2223 until at least 2.9 Ga. The font size of the letter roughly indicates the relative size of the
 2224 absorption cross section of the indicated pigment.
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Figure 4. Timeline demonstrating the correlation between the prevailing surface solar spectrum and the appearance and distribution of organic pigments. Major milestones in the evolution of life are also noted in the figure.

Common pigments to all 3 domains of life	Absorbance maximum (nm)	Molar extinction coefficient (cm⁻¹M⁻¹)
Adenine ^a	261	13400
Guanine ^a	243, 272.75	10700, 13170
Thymine ^a	263.8	7900

Cytosine ^a	266.5	6100
Uracil ^a	258.3	8200
Phenylalanine ^b	257.5	195
Tyrosine ^b	274.2	1405
Tryptophan ^b	278	5579
Histidine ^b	211	5700
Thiamine ^c	235, 267	11300, 8300
Riboflavin ^d	263, 346, 447	34845, 13751, 13222
Folic acid ^e	256, 283, 368	26900, 25100, 9120
Nicotinamide ^f	262	2780
Pyridoxine ^g	253, 325	3700, 7100
Ubiquinone-10 ^h	275	14240
Phytomenadione ⁱ	248, 261, 270	18900, -, -
Hydroxocobalamin ^j	277.75, 361, 549.75	15478, 27500, 8769
Heme A ^k	430, 532, 584	118000, 8200, 27000

2232

2233 **Table 1.** Molar extinction coefficients at maximum absorption of the nucleobases, aromatic
2234 amino acids and organic heterocyclic and aromatic cofactors common to all three domains of
2235 life.

2236 ^a Fasman, 1975; Callis, 1979; Du et al., 1998; Dixon et al., 2005

2237 ^b Fasman, 1976; Du et al., 1998; Dixon et al., 2005

2238 ^c Sigma-Aldrich, product information

2239 ^d Koziol, 1966; Du et al., 1998; Dixon et al., 2005

2240 ^e Sigma, product information

2241 ^f McLaren et al., 1973

2242 ^g Glick, 1964

2243 ^h Podda et al., 1996

2244 ⁱ Suttie, 2009; Nollet, 2012

2245 ^j Hill et al., 1964; Pratt and Thorp, 1966; Fugate et al., 1976; Du et al., 1998; Dixon et al., 2005

2246 ^k Caughey et al., 1975