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Fundamental molecules of life are pigments which arose and evolved to dissipate the solar spectrum

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Abstract

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

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1 Introduction

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

Many of the earliest organic molecules, those common to all three domains of life (Bacteria, Archaea and Eukaryote), are pigments which absorb light in the far ultraviolet (UVC-UVB) and when in an aqueous environment dissipate this light efficiently into heat. Over the history of life on Earth, organic pigments have evolved to absorb in the range where water does not, approximately 220 to 700 nm. Stomp et al. (2007) have, in fact, demonstrated just how neatly organic pigments are filling photon niches left by water. From this thermodynamic perspective, the origin of life began with the photochemical formation of organic pigments to dissipate the solar photon potential arriving at Earth's surface where water does not absorb. Specifically, we have postulated (Michaelian, 2009, 2011) that life began dissipating UVC photons within the range of 240 to 280 nm, where a window existed in the primitive Earth atmosphere (Sagan, 1973) and where the primary molecules, those common to all three domains of life (RNA and DNA, the aromatic amino acids, and enzymatic cofactors) absorb and dissipate strongly when in water.

This "thermodynamic dissipation theory for the origin of life" suggests that the evolutionary trajectory of life on Earth is, and always was, driven by increases in the global photon dissipation rate of the biosphere. This is obtained through optimizing the pigment photon dissipation at the entropically most important photon wavelengths (short wavelengths) arriving at Earth's surface by evolving; (1) increases in the photon absorp-

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age of a G0-V type star are given. From the figure it can be seen that our sun at 500 Ma (at the probable beginnings of life on Earth at 3.85 Ga), would have been 5 to 80 times (depending on wavelength) more intense at these very short wavelengths.

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

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

where σ is the Stefan-Boltzmann constant.

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

2.2 Evolution of the transparency of Earth's atmosphere

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

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was shown to be the factor most correlated with the chemical composition of the products. Aerosol production was seen to be maximum at C/O ratios close to 1, which according to Lowe and Tice (2004) would have occurred at approximately 2.9 Ga. Approximately spherical particles were found in the experiments with average diameters of about 50 nm. Particles of this size, at the estimated photochemical production rates, would have produced an optically thick layer in the UV but a rather thin layer in the visible (Trainer et al., 2006). However, as observed on Titan, and in laboratory experiments employing an electrical discharge source, these particles readily form fractal aggregates of size > 100 nm, consistent with observations of the atmosphere of Titan, thereby increasing significantly the visible attenuation with respect to the UV (Trainer et al., 2006).

Given the intensity of the Lyman- α line (121.6 nm) from hydrogen in the sun at Earth's upper atmosphere and the probable concentrations of CH_4 at these altitudes, Trainer et al. (2006) estimate an aerosol production rate on early Earth of between 1×10^{13} and 1×10^{15} g year^{-1} , which is comparable to, or greater than, the estimated delivery of pre-biotic organics from hydrothermal vents and comet and meteorite impacts combined.

By studying the sulfur isotope record, Domagal-Goldman et al. (2008) suggest that a thick organic haze, which blocked UV light in the 170–220 nm range from the photolysis of SO_2 in the lower atmosphere, arose at 3.2 Ga and persisted until 2.7 Ga. Based on these isotope ratios, they suggest that Earth's atmosphere went from a hazeless to thick haze between 3.2 and 2.7 Ga, and then again to a thin haze after 2.7 Ga. The appearance of the haze may be associated with the appearance of methanogens (and anoxygenic photosynthesizers) around 3.2 Ga, which led to a buildup of CH_4 , while continent erosion led to a decline in CO_2 , and as the ratio of CH_4/CO_2 became close to one, the organic haze became thicker and spread over the upper atmosphere.

A new study (Crowe et al., 2013) suggests that there were appreciable levels of atmospheric oxygen (3×10^{-4} times present levels) about 3 billion years ago, more than 600 million years before the Great Oxidation Event and some 300–400 million

years earlier than previous indications for Earth surface oxygenation. The researchers suggest that the observed levels are about 100 000 times higher than what can be explained by regular abiotic chemical reactions in Earth's atmosphere and, therefore, the source of this oxygen was almost certainly biological.

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

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

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

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stages, and we chose six basic stages which roughly correlate with particular geological eons supporting particular atmospheric transparencies.

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

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

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

These properties would have given them excellent entropy producing capacity. It is, therefore, probably not a coincidence that the fundamental molecules of life (nucleic acids, aromatic amino acids, enzymatic cofactors) are actually organic pigments in the UVC-UVB range. These molecules, that are at the foundations of life today, could have floated on the surface of the primordial ocean in monomeric or single strand polymeric

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form, absorbing and dissipating UV and visible solar photons, transferring this energy to surrounding water molecules and enhancing in this manner the early water cycle and Earth's global entropy production in its solar environment (Michaelian, 2012a).

In support of this conjecture is the fact that the five naturally occurring nucleic bases (adenine, guanine, thymine, cytosine, uracil) are UV-pigments which absorb in the 240–290 nm UV region, the short wavelength part of the solar spectrum which could have penetrated Earth's early Hadean and Archean atmosphere (Sagan, 1973), dissipating this radiation into heat with subpicosecond singlet excited state lifetimes (Pecourt et al., 2000; Middleton et al., 2009). Another interesting and corroborating fact is that their non-natural tautomers have much longer decay times (Serrano-Andrés and Merchán, 2009; Gustavsson et al., 2006; Crespo-Hernández et al., 2004) implying much lower entropy producing efficacy and photochemical stability. Furthermore, it has been demonstrated that the guanine-cytosine Watson-Crick base pairs exhibit superior photon-dissipation characteristics compared to other possible base pairing between these nucleobases (Abo-Riziq et al., 2005). Woutersen and Cristalli (2004) have found that vibrational relaxation of the NH-stretching mode occurs much faster in the adenine-uracil Watson-Crick base pairs compared to isolated monomeric uracil and that the hydrogen bonding between these bases is responsible for the extremely fast vibrational relaxation in the base-pair system. Therefore, the coupling of nucleobase photon dissipation to the water cycle and the resulting increase in entropy production can be seen as the thermodynamic driving force for their polymerization into RNA/DNA and the ensuing replication of these polymers through an ultraviolet and temperature assisted RNA/DNA reproduction (UVTAR; Michaelian, 2009, 2011).

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

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

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

Pigment-catalyzed evaporation may have led to increased concentration of organics and ions in the sea surface layer thus promoting molecular interactions. In this manner an early association through chemical affinity between the replicating nucleic acids and

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other pigment molecules is plausible. Yarus et al. (2009) have provided experimental evidence for a stereochemical era during the evolution of the genetic code, relying on chemical interactions between amino acids and the tertiary structures of RNA binding sites. According to their results a majority (approximately 75 %) of modern amino acids entered the code during this stereochemical era; nevertheless, only a minority (approximately 21 %) of modern codons and anticodons retain clear vestiges of these original RNA binding sites. Interestingly, the binding site for the aromatic amino acid tryptophan is among the simplest of the amino acid binding sites known, as well as selective among hydrophobic side chains, and there is a recurring CCA sequence (a tryptophan anticodon triplet) which apparently forms one side of the binding site (Majerfeld and Yarus, 2005). Moreover, Polyansky and Zagrovic (2013) have provided strong evidence for the stereochemical foundation of the genetic code and suggest that mRNAs and cognate proteins may in general be directly complementary to each other and associate, especially if unstructured. Their results show that of all 20 proteinogenic amino acids, tryptophan has the highest binding affinity for purines, and histidine has the highest binding affinity for pyrimidines, followed by phenylalanine and tyrosine.

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

Mayer et al. (1979) have tested oligopeptides containing tyrosyl, lysyl, and alanyl residues which bind to polynucleotides and found that tyrosyl fluorescence of the peptides is quenched in their complexes with both single-stranded and double-stranded nucleic acids. An energy transfer mechanism from tyrosine to nucleic acid bases was proposed to account for fluorescence quenching in oligopeptide complexes with double-

stranded DNAs. They further theorize that due to the specificity of its stacking interaction for single-stranded nucleic acid structures, tyrosine might be involved through such interactions in the selective recognition of single strands by proteins.

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

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

The cooling of the ocean at the beginning of the Archean probably became the second major selective force after photon dissipation in organic pigment evolution, which induced further association of the aromatic amino acids and other pigment molecules with DNA or RNA and growth in complexity of these structures. In order for denaturing, replication and resulting proliferation of the UV-absorbing DNA/RNA polymers to persist in ever colder waters, their auxiliary set of light-harvesting antenna pigments (small peptides and cofactor molecules) had to enlarge and grow in complexity by acquiring primitive enzymatic functions. Michaelian (2011) argues how thermodynamic driving forces of maintaining and even incrementing entropy production in ever colder seas most probably instigated the appearance of information content on RNA/DNA and the associated need for their reproductive fidelity. Toulmé et al. (1974) have shown how tryptophan-containing peptides might have played an enzymic role in the maintenance of this fidelity by acting as primitive photolyase enzymes. Goldfarb et al. (1951) have

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estimated that each peptide bond contributes an average of about 2500 to 2800 to the molar absorption coefficient of proteins at 250 nm, and this was probably the thermodynamic reason for the pre-biotic synthesis of polypeptides and their association with RNA and DNA under high UVC-UVB light conditions of the early Archean.

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

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

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

Ancient (3.2–3.6 Ga) sedimentary rocks from the Barberton Greenstone Belt in South Africa and Swaziland and the Pilbara Craton in Western Australia have been found to contain prokaryotic microfossils (Noffke et al., 2013; Schopf, 2006). Evidence in these rocks suggests that 3.5 Ga old prokaryotic microorganisms flourished in the form of microbial mats and stromatolites. Stromatolites represent accretionary sedimentary

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structures from shallow water environments, produced by the activity of prokaryotic, photoautotrophic microorganisms, living in mucilage-secreting communities known as microbial mats (Schopf, 2006).

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

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

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

From the optics of the thermodynamic dissipation theory for the origin and evolution of life (Michaelian, 2009, 2011), and the established facts given above, a picture

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of life on Earth prior 3.5 Ga can be inferred. From the multitude of different pigment complexes, the one that gave rise to the line of the LUCA evolved to be a prokaryote-like, lipid-membrane vesicle (protocell) where the “old generation” of UV-dissipaters (DNA/RNA, some proteins) began to take on a new secondary role of information-carriers and chemical catalysts, becoming genetic material, ribosomes and enzymes, with a new function – to execute the synthesis, support, and proliferation of the “new dissipating generation of pigments” more completely covering the evolving solar spectrum available at Earth’s surface.

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

Many Urey-Miller-type experiments, using various sources of energy, have readily produced oligopyrroles and porphyrins abiotically, including using electrical discharges (Hodgson and Ponnampertuma, 1968; Simionescu et al., 1978), ultraviolet irradiation (Szutka, 1965; Hodgson and Baker, 1967; Meierhenrich et al., 2005), temperature of 70–100 °C, compatible with a prebiotic milieu (Lindsey et al., 2009). Porphyrin-like substances have even been found in meteorites (Hodgson and Baker, 1964) and Precambrian rocks (Kolesnikov and Egorov, 1977). Porphyrins have a chemical affinity to DNA, their plane intercalates into DNA or they form stacked aggregates on its surface (Pasternack et al., 1991, 1993; Pasternack and Gibbs, 1996).

different metabolic subnetworks, of which “porphyrin and chlorophyll metabolism” has been shown to be the most ancient (Caetano-Anollés et al., 2012).

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

Chlorophyll, common in most modern phototropic organisms, plays essentially this dissipative role. Since it has two excitation levels (the high energy Soret band in the near UV and the low energy Qy band in the red) the dissipation of a photon with transition from the Soret to the Qy band is extremely efficient. Enhancement and redshift of the Qy band would provide even more efficient photon dissipation and this is indeed a recognizable trait in the proposed evolutionary trajectory from protoporphyrin IX via protochlorophyll *c* to chlorophyll *c* and then to chlorophyll *a* (Olson and Pierson, 1987; Larkum, 1991).

Mulkidjanian and Junge (1997) further theorize how at the beginning this dissipative photochemical activity in the cell functioned only in the context of UV-“protection”, but later mutations, which caused the loss of certain pigment components, led to obtainment of redox cofactors and a gradual transition from purely dissipative to productive photochemistry, i.e. from UV-“protection” to photosynthesis. In the context of the thermodynamic dissipation theory for the origin of life, this putative pigment-carrying membrane protein, instead of being an “ancient UV-protector” is more appropriately designated as the “new generation” of UV-dissipating pigments, continuing, from the nucleic

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and amino acids, the thermodynamic role of photon dissipation and catalysis of the water cycle. Since porphyrin/chlorin-carrying proteins are universal to all three domains of life (Georgopapadakou and Scott, 1977; Suo et al., 2007), either as chlorophyll-carrying photosystems, or heme-carrying cytochromes, it is quite plausible that this primordial porphyrin-protein complex was the main dissipating unit of the LUCA protocells.

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

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

There is a continuity of stromatolites in the fossil record from 3.5 to 2.5 Ga, even though Archean geological units are relatively scarce when compared to those of the Proterozoic (Schopf et al., 2007). The distribution of Archean stromatolites seems to consistently parallel the estimated temporal distribution of Archean sediments that have survived to the present, in a way that most stromatolite fossils have been reported from younger rocks (2.5–3.0 Ga) relatively abundant in the fossil record, and fewer from older rocks (3.5–3.0 Ga) relatively scarce in the fossil record. Biogenicity of these sediments has been backed by the discovery of microscopic fossils with microbe-like morphologies typical of later, less questionable Proterozoic microfossils: sinuous tubular or unis-

eriate filaments, small rod-shaped bodies, or unornamented coccoids (Schopf, 2006). Geochemical evidence from the Buck Reef Chert (250 to 400 m thick rock running along the South African coast) show that it was most likely produced by the activities of phototrophic microbial communities about 3.4 billion years ago (Tice and Lowe, 2004, 2006). The same authors characterize the inhabitants of these ancient microbial communities as partially filamentous phototrophs which probably used the Calvin–Benson–Bassham cycle for CO₂ fixation according to local carbon isotope composition. Interestingly, they failed to notice any traces of life in the deeper (> 200 m) aquatic environments.

Combining this evidence with the results of Crowe et al. (2013) for the beginnings of atmosphere oxygenation would indicate that the advent of oxygenic photosynthesis was sometime prior 3 Ga, and was carried out by cyanobacteria-like organisms usually referred to in the scientific community as protocyanobacteria (Olson, 2006; Garcia-Pichel, 1998).

Cyanobacteria are believed to be one of the most ancient groups of organisms on this planet and among the earliest to branch off in a separate phylum (Altermann and Kazmierczak, 2003). As the only prokaryotes which carry out oxygenic photosynthesis, there is little doubt among scientists today that they were responsible for the production and accumulation of oxygen and ozone in the atmosphere (Bekker et al., 2004). Oxygenic photosynthesis is distinguished by the presence of two photosystems (photosystem I and photosystem II) of which photosystem II incorporates the water-splitting complex (four oxidized manganese atoms and a calcium atom, held in place by proteins), and the utilization of water as a reductant, which generates oxygen as a waste product (Kiang et al., 2007; Allen and Martin, 2007). In contrast, anoxygenic types of photosynthesis employ only one of the photosystems (photosystem I or photosystem II), but never both, lack the water-splitting complex and utilize other electron donors: hydrogen, hydrogen sulfide, ferrous ions, nitrite etc. (Kiang et al., 2007; Bryant and Frigaard, 2006).

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

Besides protocyanobacteria and other members of the domain Bacteria, the Archean seas were most likely also harboring the ancestors of modern domain Archaea (Wang et al., 2007; Woese and Gupta, 1981). If the ancestors of cyanobacteria were already present by 3 Ga, it is sensible to conclude that the line of the LUCA had already branched into the separate domains Bacteria and Archaea at a much earlier point in time, probably as early as 3.5 Ga, or even earlier. No known member of the Archaea domain carries out photosynthesis, although some members of the class Halobacteria are photoheterotrophs which utilize light energy absorbed by the chromoprotein bacteriorhodopsin to synthesize ATP, and their carbon source is organic (Bryant and Frigaard, 2006). Mulkidjanian and Junge (1997) hypothesize that the bacteriorhodopsin-based phototropism in Archaea might have also evolved from a “UV-protecting” precursor function, because it has been shown (Kalisky et al., 1982) that a UV-quantum, channeled from the aromatic amino acid residues of the protein moiety, triggers the *all-trans* to 13-cys isomerization of the retinal moiety in bacteriorhodopsin, followed by its return into the initial isomeric state by slow thermal relaxation. This bacteriorhodopsin-based photon dissipation in Archaea probably evolved as a complementary to the chlorophyll-based in protocyanobacteria for dissipation of visible wavelengths left unabsorbed by chlorophyll (DasSarma, 2006, 2007).

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Phylogenetic analyses, however, show that the common ancestor of cyanobacteria and chloroplasts had both chlorophyll *b* and phycobilins (Tomitani et al., 1999). The antiquity of chlorophyll *b* and its early presence in the protocyanobacterial lineage might be backed by the fact that it has an absorption peak in the UVC at around 258 nm (Zalar et al., 2007).

Shales of the early Mesoproterozoic Roper Group in northern Australia have been found to contain 1.5 Ga old organic fossils called acritarchs which are suspected to be unicellular eukaryotes and most probably algae by virtue of preserved cell wall and cytoskeletal structures (Javaux et al., 2001). Already by 1.2 Ga very modern-looking and well-preserved fossils of red algae start appearing in the fossil record (Butterfield, 2000), although more recent work proposes the existence of even older fossils of filamentous algae dating back as far as 1.6 to 1.7 Ga (Bengtson et al., 2009).

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

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

inducible polypeptides (HLIPs), which are not involved in photosynthesis and simply accumulate in the cell in response to intense light exposure and dissipate this energy to heat (Havaux et al., 2003; Montane and Kloppstech, 2000). This behavior has led biologists to ascribe a photo-protective role to this class of pigmented polypeptides, although we believe that their function might be more accurately described from the thermodynamic viewpoint as dissipaters of light and catalysts of the hydrologic cycle.

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

The relatively rapid emergence and diversification of many new phyla and species of animals during the Cambrian period (542–488 Ma) is known as the Cambrian explosion or Cambrian radiation (Erwin and Valentine, 2013; Knoll and Carroll, 1999). The oldest unequivocal fossils of land plants and fungi date from the late Cambrian period, around 480–460 Ma, but molecular evidence suggests that they may have colonized the land much earlier than previously thought, even before the Cambrian Explosion and Snowball Earth events (Heckman et al., 2001). The spread of the organic pigments to land and their fomentation of a terrestrial water cycle extending ever more inland, provided the potential for another 30 % of Earth's surface area to be cultivated for photon dissipation.

Land plants evolved from chlorophyte algae living in shallow fresh waters, perhaps as early as 510 million years ago (Raven and Edwards, 2001); some molecular estimates place their origin even earlier, as much as 630 million years ago (Clarke et al., 2011). Their chloroplasts contain the visible-absorbing pigments: chlorophyll *a* and *b*, different carotenes and xanthophylls, collectively known as photosynthetic pigments (Ruban, 2012); and the visible- and UV-absorbing flavonoids, which are phenolic secondary plant metabolites that do not participate in photosynthesis and are traditionally given UV-protective and antioxidant roles (Gould and Lister, 2006; Agati et al., 2007). Anthocyanins are flavonoid, water-soluble, vacuolar pigments, biosynthetically derived from phenylalanine, which occur in all tissues of higher plants, including leaves, stems,

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et al. (2013) have shown how the Pleistocene Amazonian megafauna extinctions dramatically decreased the lateral flux of nutrients (particularly of phosphate) in all continents outside of Africa. Lavery et al. (2010) have determined that blue whales feces contribute enormously to the distribution of iron in the Southern Ocean for the proliferation of cyanobacteria and thus photon dissipation in mid ocean environments, and even for the sequestering of atmospheric carbon, the latter a very modern preoccupation.

4 The organic pigment tree of life correlates with the history of Earth's surface spectrum

Utilizing the data presented in Sect. 2 for the abiotic and biotic events affecting Earth's atmosphere, and assuming a black-body spectrum for the sun in the relevant wavelength region, a coarse grained history of the solar spectrum at Earth's surface can be derived. The calculations presented below assume a present day black-body solar photosphere at an effective temperature of 5840 K with an H^- stellar atmosphere absorption line centered on 500 nm, and includes the time dependence of the increase in the solar radius and increase in surface temperature as considered in Sect. 2.1 above. The results of the calculation are presented below and in Figs. 2 and 3 within the relevant time intervals.

Before the origin of life at 3.85 Ga and until about 3.2 Ga, the solar spectrum on Earth included a unique region of between approximately 230 and 290 nm of an integrated flux of $5.5 \pm 2 \text{ W m}^{-2}$ midday at the equator with the spectral distribution in this region peaking at around 260 nm, bounded on the short wavelength side by H_2S absorption and on the long wavelength side by formaldehyde and acetaldehyde (both photochemical reaction products of UV on hydrogen sulfide). From 290 to about 320 nm, little light would have been available on the surface due to absorption by the aldehydes. Beyond 320 up to 700 nm, where the water absorption becomes important (a warmer Earth would have supported a more humid atmosphere), the spectrum at Earth's surface in the Archean was probably very similar to the present day spectrum but of about 30%

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lower luminosity due to a faint young sun, providing an integrated energy flux of approximately 327 W m^{-2} integrated over 320 to 700 nm midday at the equator. The biological world in this era consisted of the dominance of UVC-UVB-dissipating pigments in protocells, among them LUCA, and included the split of the line of the LUCA into Bacteria and Archaea and the early branching of the protocyanobacterial line within Bacteria.

From 3.2 to 2.7 Ga, a thick upper atmosphere organic haze probably existed due to the rise of the methanogens, bringing the CH_4/CO_2 ratio close to one, which is the condition for haze production (Lowe and Tice, 2004). The wavelength dependence of the resulting albedo would depend on the size of the agglomerates formed in the atmosphere, probably increasing that of longer wavelengths by a relatively greater amount (as on Titan today; McGrath et al., 1998), but would have generally increased the albedo at all wavelengths with an ensuing cooling of Earth's surface locally to glacier temperatures. The biosphere saw the branching of oxygenic cyanobacteria within the protocyanobacterial line and the beginning of gradual O_2 accumulation with the continuing dominance of UV-dissipating pigments but the visible pigments rising in importance.

From about 2.7 to 2.45 Ga the organic haze produced by UVC light on CH_4 in the upper atmosphere began to decline as erosion of the continents and tectonic recycling of CO_2 reduced the CH_4/CO_2 ratio, thereby increasing the intensity of the spectrum at Earth's surface between 320 and 700 nm while at the same time ozone, resulting from oxygenic photosynthesis, was beginning to reduce the intensity of the UV spectrum between 230 to 290 nm. Dissipation in this wavelength range was now becoming ever more relegated to life derived ozone in the upper atmosphere. The biosphere was seeing the diversification of cyanobacteria and the appearance of multicellular forms of cyanobacteria, increasingly dissipating in the visible.

After about 2.45–2.2 Ga ozone from oxygenic photosynthesis would have reduced light within the 230–290 nm wavelength range to less than perhaps a few percent of its value at the beginnings of life ($5.5 \pm 2 \text{ W m}^{-2}$ at 3.85 Ga). The biosphere was ex-

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perienicing the endosymbiosis of mitochondria and chloroplasts and the emergence of eukaryotes. Visible-dissipating pigments probably became dominant in this era.

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

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

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

For the spectrum calculation at present day, 0.0 Ga, we include absorption of oxygen at 21 %, ozone absorption and Rayleigh scattering at present atmospheric pressures giving an integrated energy flow of 865 W m⁻² midday at the equator, consistent with measured values (Gates, 1980).

The calculations presented in Figs. 2 and 3 have internal consistency with; an increase of about 27 % in the integrated energy flow arriving at the top of Earth's atmosphere since the beginnings of life; a total of 865 W m⁻² arriving at Earth's surface with 9 % of the energy flow in the ultraviolet below 400 nm today. Results for the beginning of life (3.85 Ga) are 5.5 W m⁻² within the 230–290 nm region arriving at Earth's surface and 4.3 W m⁻² within the reduced wavelength 240–270 nm region, roughly consistent with Sagan's (1973) calculation of 3.3 W m⁻².

Figure 3 plots the chromophoric fundamental molecules of life (first organic pigments) which are common to all three domains of life (see Table 1) at their absorp-

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leading to complex organic pigments which are fundamental molecules of life including RNA, DNA, aromatic amino acids, organic cofactors, quinones and porphyrins.

These fundamental bio-molecules, common to all three domains of life, absorb and dissipate strongly within the UVC-UVB range of 230 to 290 nm, especially when intercalated or coupled externally to RNA and DNA which acts as a quencher molecule. A non-linear, non-equilibrium thermodynamic directive suggests a spontaneous proliferation of these dissipating molecules to concentrations much greater than their expected near equilibrium concentration over the entire surface of the Earth exposed to this radiation. The proliferation of these molecules to high concentrations and their global dispersion can be explained by the fact that the photochemical production of these pigments is an autocatalytic reaction process established to dissipate the solar photon potential (Michaelian, 2013). The proliferation and evolution of these pigment molecules over time, which succinctly characterizes all biological and even coupled biotic-abiotic evolution (Michaelian, 2012b), can best be described through five basic tendencies; to increase the ratio of their effective photon absorption cross sections to their physical size, to decrease their electronic excited state life times, to quench radiative de-excitation channels (e.g. fluorescence), to cover ever more completely the prevailing solar spectrum, and finally to disperse over an ever greater surface area of Earth. The appearance of mobile protozoa and animals can be seen as fomenting this thermodynamic directive by providing the vehicle of dispersion with the overall objective of increasing the global entropy production of Earth in its solar environment.

These fundamental molecules today have lost their direct dissipating utility and are produced only through complex enzymes and metabolic reaction pathways; however, they are still completely relevant in their supportive role that they play in fomenting the proliferation and dispersion over Earth's surface of the contemporary dissipating pigments in the visible.

This is important evidence in support of the thermodynamic dissipation theory of the origin of life (Michaelian, 2009, 2011) which states that life arose and proliferated to carry out the thermodynamic function of dissipating the entropically most important part

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of the solar spectrum (the shortest wavelength photons) prevailing at Earth's surface and that this irreversible process began to evolve and couple with other irreversible abiotic processes, such as the water cycle, to become more efficient, to cover ever more of the electromagnetic spectrum, and cover ever more of Earth's surface. This

dissipation continues today as the most important thermodynamic function performed by living organisms as part of a greater dissipating system known as "the biosphere" (Michaelian, 2012b).

Our conjecture provides a new avenue for exploration of Earth's ancient atmosphere based on pigment history analysis. For example, the lack of primordial pigments absorbing between 290 and 320 nm strongly suggest the presence of aldehydes in the Archean atmosphere as postulated by Sagan (1973). Finally, our conjecture sheds new light on the origin of photosynthesis. The demonstrated abiotic production of porphyrins using UV light and their UVC-UVB absorption and dissipation characteristics when stacked as agglomerates and intercalated or coupled externally to RNA or DNA, suggests that photosynthesis arose as an adjunct to the porphyrins UV light-harvesting and dissipation function, as postulated by Mulikdjanian and Junge (1997), when the photochemically active light at Earth's surface began to wane as life produced ozone took on the dissipative role at these wavelengths in the upper atmosphere. Photosynthetic proliferation at visible wavelengths then superseded UVC dissipative autocatalytic proliferation. A greater in depth analysis remains to be performed on the relation between RNA/DNA and the porphyrins and that between dissipation and photosynthesis and we are presently engaged in experiments to explore these ideas.

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

| Common pigments to all 3 domains of life | Absorbance maximum (nm) | Molar extinction coefficient ($\text{cm}^{-1}\text{M}^{-1}$) |
|--|-------------------------|--|
| Adenine ^a | 261 | 13 400 |
| Guanine ^a | 243, 272.75 | 10 700, 13 170 |
| 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 | 11 300, 8300 |
| Riboflavin ^d | 263, 346, 447 | 34 845, 13 751, 13 222 |
| Folic acid ^e | 256, 283, 368 | 26 900, 25 100, 9120 |
| Nicotinamide ^f | 262 | 2780 |
| Pyridoxine ^g | 253, 325 | 3700, 7100 |
| Ubiquinone-10 ^h | 275 | 14 240 |
| Phytomenadione ⁱ | 248, 261, 270 | 18 900, –, – |
| Hydroxocobalamin ^j | 277.75, 361, 549.75 | 15 478, 27 500, 8769 |
| Heme A ^k | 430, 532, 584 | 11 8000, 8200, 27 000 |

^a Fasman (1975); Callis (1979); Du et al. (1998); Dixon et al. (2005)

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

^c Sigma-Aldrich, product information

^d Koziol (1966); Du et al. (1998); Dixon et al. (2005)

^e Sigma, product information

^f McLaren et al. (1973)

^g Glick (1964)

^h Podda et al. (1996)

ⁱ Suttie (2009); Nollet (2012)

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

^k Caughey et al. (1975)

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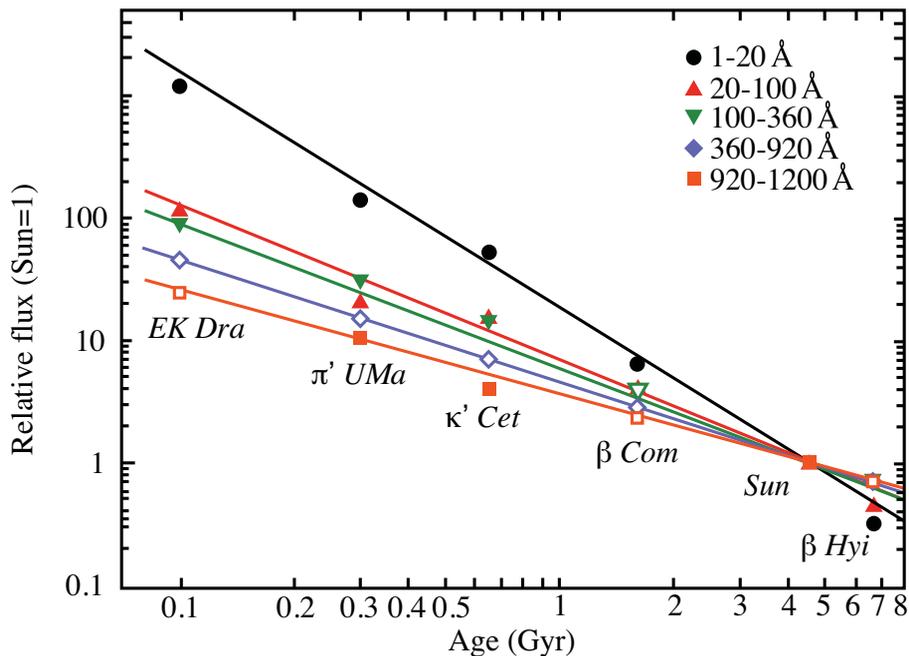


Figure 1. Solar-normalized fluxes (with respect to those of today) vs. stellar age for different wavelength bands for solar-type stars. Taken from Ribas et al. (2005).

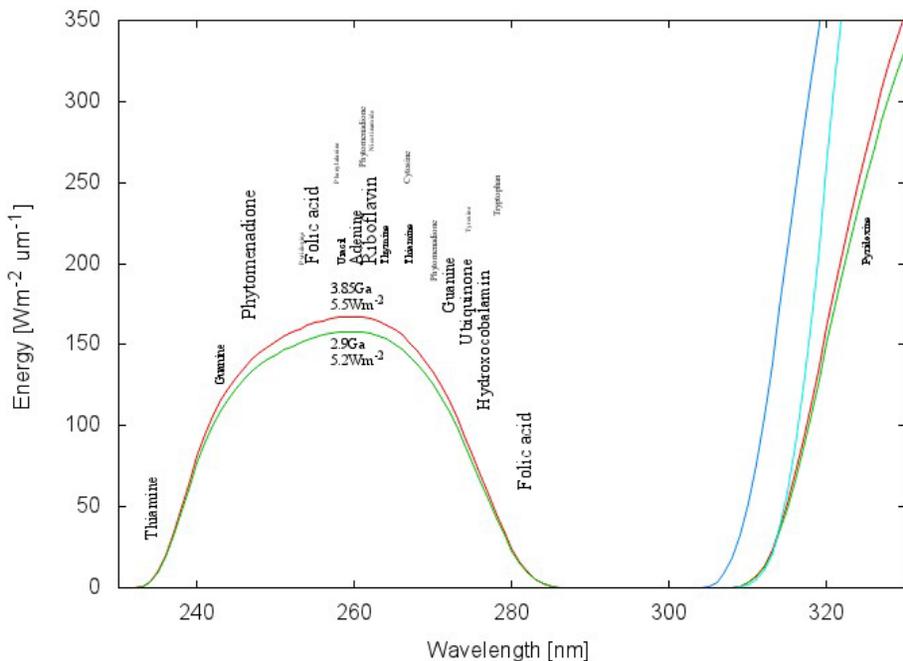


Figure 3. The wavelengths of maximum absorption of many of the fundamental molecules of life (common to all three domains) coincide with the predicted solar spectrum at Earth's surface in the UVC at the time of the origin of life at 3.85 Ga and until at least 2.9 Ga. The font size of the letter roughly indicates the relative size of the absorption cross section of the indicated pigment.

Life's fundamental molecules dissipated solar spectrum

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