Properties of cyanobacterial UV-absorbing pigments suggest their evolution was driven by optimizing photon dissipation rather than photoprotection

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Abstract

An ancient repertoire of ultraviolet (UV)-absorbing pigments which survive today in the phylogenetically oldest extant photosynthetic organisms, the cyanobacteria, point to a direction in evolutionary adaptation of the pigments and their associated biota; from largely UV-C absorbing pigments in the Archean to pigments covering ever more of the longer wavelength UV and visible in the Phanerozoic. Such a scenario implies selection of photon dissipation rather than photoprotection over the evolutionary history of life. This is consistent with the thermodynamic dissipation theory of the origin and evolution of life which suggests that the most important hallmark of biological evolution has been the covering of Earth’s surface with organic pigment molecules and water to absorb and dissipate ever more completely the prevailing surface solar spectrum. In this article we compare a set of photophysical, photochemical, biosynthetic and other germane properties of the two dominant classes of cyanobacterial UV-absorbing pigments, the mycosporine-like amino acids (MAAs) and scytonemin. Pigment wavelengths of maximum absorption correspond with the time dependence of the prevailing Earth surface solar spectrum, and we proffer this as evidence for the selection of photon dissipation rather than photoprotection over the history of life on Earth.
1 Introduction

Once the subject of mystical and metaphysical interpretations, the explanation of life on Earth has slowly gained a physical-chemical grounding in biochemistry and non-equilibrium thermodynamics. Founded on Boltzmann’s nineteenth century insights into thermodynamics, then further elaborated by twentieth century scientists, notably by Ilya Prigogine, non-equilibrium thermodynamics attempts to explain the phenomenon of life as “dissipative structuring”; an out of equilibrium organization of matter in space and time under an impressed external potential for the explicit purpose of producing entropy (Prigogine, 1967; Glansdorff and Prigogine, 1971).

Using the formalism of Prigogine’s “Classical Irreversible Thermodynamics” in the non-linear regime, Michaelian (2009; 2011; 2012; 2013; 2016) has proposed a theory for life’s origin and evolution as microscopic self-organized dissipative structuring of organic pigment molecules and the dispersal of these over the entire surface of the Earth as a response to the impressed high-energy (UV-C to visible) solar photon spectrum prevailing at Earth’s surface. All physicochemical structuring associated with the pigments, such as the photosynthetic organisms primarily, and heterotrophic organisms secondarily, can be regarded as agents for the synthesis, proliferation and distribution of the pigments. The theory suggests that it is the thermodynamic imperative of increasing the entropy production of Earth in its solar environment that is behind the vitality of living matter as seen in its ability to proliferate, diversify, and evolve.

The theory explains satisfactorily, for example, why the three major classes of photosynthetic pigments (chlorophylls, carotenoids and phycobilins) of phototrophic organisms dissipate most of the absorbed photonic energy into heat (a process known as non-photochemical quenching, NPQ) while funneling only a minute fraction into productive photochemistry (Horton et al., 1996; Ruban et al., 2007; Staleva et al., 2015; Gupta et al., 2015). Moreover, these organisms often contain a vast array of other organic pigments in addition to the photosynthetic ones, whose absorption spectra extend outside of the photosynthetically active radiation (PAR) in the visible, and into the UV-A, UV-B, and UV-C regions, hence allowing full coverage of the past and present incident surface solar spectra (Michaelian, 2012; Michaelian and Simeonov, 2015). In the biological literature these phenomena have been explained primarily through invoking the conventional wisdom of photoprotection (Demmig-Adams and Adams, 1992; Mulkidjanian and Junge, 1997; Wynn-Williams et al., 2002; Mulkidjanian et al., 2003; Castenholz and Garcia-Pichel, 2012).

Photoprotective roles have especially been attributed to UV-absorbing biological pigments (e.g., mycosporine-like amino acids and scytonemins in cyanobacteria and algae; flavonoids and anthocyanins in plants, etc.) since they don’t seem to contribute to photosynthesis at all (Moisan and Mitchell, 2001). These theories usually trace the photoprotective role of UV-pigments back to the beginnings of cellular life in the early Archean when UV radiation was far more important component of the surface solar spectrum than it is today (Sagan, 1973; Mulkidjanian and Junge, 1997; Garcia-Pichel, 1998; Cockell and Knowland, 1999; Mulkidjanian et al., 2003). UV-screening ostensibly conferred pigment-containing organisms Darwinian advantages for survival in the harsh Archean environment of intense UV
radiation.

However, from a thermodynamic viewpoint, the UV is the region of the solar spectrum with the greatest possible entropy production potential per unit photon dissipated. Therefore, under the high UV ambient conditions of our primitive planet, non-equilibrium thermodynamic principles of increasing the entropy production of Earth in its solar environment were probably the motive force for the development of these microscopic dissipative structures in the form of efficient UV-dissipating organic compounds (Michaelian, 2011; 2013), rather than metaphysical forces giving rise to a hypothetical “will to survive” of the individual cell. The evidence for this inextricable link between UV light and nascent life has been reinforced with the verifications for biogenicity of ~3.5 Ga old euphotic stromatolitic formations (Walter et al., 1980; Awramik et al., 1983; Schopf and Packer, 1987; Schopf, 1993; Schopf et al., 2002; Tice and Lowe, 2004; Van Kranendonk et al., 2008) of evidently photosynthetically active, yet UV-C bathed, microbial colonies of cyanobacteria-like organisms (Westall et al., 2006; Westall, 2009). If confirmed, an approximately 3.7 Ga old putative stromatolite from an Eoarchean shallow marine environment (Nutman et al., 2016) would make this fossil the oldest evidence for complex life thriving on Earth under intense UV light.

In this paper we discuss how the two major classes of cyanobacterial UV-absorbing pigments, the mycosporine-like amino acids and the scytonemins, whose occurrence in organisms today is regarded as a relic from Archean times (Garcia-Pichel, 1998), perfectly match the type of microscopic dissipative structure which non-equilibrium thermodynamic principles would predict for the Archean Earth system.

In the following section we separately detail a set of germane properties of both pigment classes, taken from the literature, whereas in the third section we demonstrate how these properties are consistent with several postulates made in a previous work (Michaelian and Simeonov, 2015). Also, in the third section, we compare the pigments’ optical properties with our previous construct of the most probable Earth surface solar spectrum as a function of time (see Michaelian and Simeonov, 2015).

Based on these comparisons we evaluate the relative antiquity of both pigment classes and show how the observed facts support the thermodynamic dissipation theory of the origin and evolution of life (Michaelian, 2009; 2011; 2012; 2016).
2 Properties of cyanobacterial UV-absorbing pigments

2.1 Mycosporine-like amino acids (MAAs)

MAAs and a related group of organic compounds called mycosporines represent a large family of colorless, low-molecular-weight (< 400 u), water-soluble, usually intracellular secondary metabolites widespread in the biological world (Dunlap and Chalker, 1986; Carreto et al., 1990; Rosic and Dove, 2011). The exact number of compounds within this family is yet to be determined, since they have only relatively recently been discovered (for a historical overview, see Schick and Dunlap, 2002 and Řezanka et al., 2004), and novel molecular species are constantly being uncovered. Thus far, however, their number is around 40 (Wada et al., 2015). The name “mycosporine” has to do with them being originally isolated and chemically identified from mycelia of sporulating fungi, where it was thought they played a role in light-induced sporulation (Leach, 1965; Trione and Leach, 1969).

2.1.1 Physicochemical properties

Chemically both MAAs and mycosporines are alicyclic compounds (see Fig. 1) sharing a central 5-hydroxy-5-hydroxymethyl-2-methoxycyclohex-2-ene ring with an amino compound substituted at the third C-atom and either an oxo or an imino functionality at the first C-atom (Favre-Bonvin et al., 1976; Ito and Hirata, 1977; Arpin et al., 1979; Karentz, 2001). While most authors don’t make a clear chemical distinction between the two groups, several authors (for example: Bandaranayake, 1998; Schick and Dunlap, 2002; Carreto et al., 2011; Moliné et al., 2014; Miyamoto et al., 2014) when using the term mycosporines refer only to those molecular species with a central amino-cyclohexenone chromophore (also called oxo-mycosporines), and when using the term MAAs refer only to molecules with a central amino-cyclohexenimine chromophore (also called imino-mycosporines). The N-substitution on C-3 with different amino acids or amino alcohols is what gives the diversity of molecular structures within both groups (Korbee et al., 2006; Sinha et al., 2007; Carreto and Carignan, 2011). Within the MAA group, the most common amino acid on the C-3 position is glycine, whereas they also have a second amino acid, amino alcohol or an enaminone system attached at the C-1 position (D’Agostino et al., 2016).

This unique molecular structuring and bonding begets their unique spectral properties. MAAs are considered to be one of the strongest UV-A/UV-B-absorbing substances in nature (Schmid et al., 2000); with wavelength absorption maxima ($\lambda_{max}$) in the 310-362 nm interval and molar attenuation coefficients ($\varepsilon$) between 28100 and 50000 M$^{-1}$cm$^{-1}$ (Dunlap and Schick, 1998; Carreto et al., 2005; Gao and Garcia-Pichel, 2011). Their absorption spectra are characterized by a single sharp $\lambda_{max}$ with a bandwidth of approximately 20 nm and only about 2-3 nm apart from the $\lambda_{max}$ of structurally similar MAAs (see Fig. 2) which makes it very difficult to distinguish these compounds based solely on their absorption spectra (Karentz, 1994; Carroll and Shick, 1996).

The values of $\lambda_{max}$ and $\varepsilon$ are dependent on the degree of derivatization of the central ring and the nature of the nitrogenous side groups (in particular the presence of additional
conjugated double bonds) (Singh et al., 2010; Wada et al., 2015). Smaller, mono-substituted mycosporines (typically oxo-mycosporines) have their $\lambda_{max}$ values shifted to shorter wavelengths in the UV-B and usually have lower $\varepsilon$ values; whereas MAAs (imino-mycosporines) are normally bi-substituted, with higher $\varepsilon$ values and $\lambda_{max}$ values shifted to longer wavelengths in the UV-A (Portwich and Garcia-Pichel, 2003).

For example, the direct metabolic precursor of all mycosporines, 4-deoxygadusol (Fig. 1), which has the minimal level of derivatization, has $\lambda_{max} = 268$ nm at acidic pH, and $\lambda_{max} = 294$ nm at basic pH; mycosporine-glycine (Fig. 1), the simplest oxo-mycosporine and direct precursor of all other mycosporines and MAAs has a $\lambda_{max} = 310$ nm, whereas palythine (Fig. 1), a simple mono-substituted MAA (amino-MAA), has $\lambda_{max} = 320$ nm and $\varepsilon = 36200$ $M^{-1}cm^{-1}$ (Carreto et al., 2005; Gao and Garcia-Pichel, 2011). Palythene (Fig. 1), a bi-substituted MAA with an additional conjugated double bond, has one of the most red-shifted bands of all known MAA species, with $\lambda_{max} = 360$ nm and $\varepsilon = 50000$ $M^{-1}cm^{-1}$ (Uemura et al., 1980).

The observed red-shift in $\lambda_{max}$ is a consequence of the degree of resonance delocalization inside the molecules; the more efficient is the electron delocalization (i.e. the stronger the $\pi$-conjugation character) the lower is the energy requirement for an electronic transition and consequently the higher are the $\lambda_{max}$ and $\varepsilon$ values (Carreto and Carignan, 2011; Wada et al., 2015).

From a thermodynamic perspective, the fate of the electronic excitation energy is also a very relevant aspect of the absorption event since it is directly linked to the amount of entropy produced by the dissipative microscopic structure (i.e. the polyatomic molecule). Nonradiative, vibrational relaxation pathways of the excited state lead to more efficient energy dissipation and higher entropy production when compared to the fluorescent or phosphorescent radiative decay channels (Würfel and Ruppel, 1985; Michaelian, 2011; 2012; 2016). In this respect MAAs prove to be very efficient dissipative structures, although all studies hitherto have discussed these thermodynamically relevant characteristics only from the standpoint of photostability and UV-photoprotection.
Aiming at fully describing their photophysical and photochemical properties and expanding the evidence on the assigned UV-photoprotective role, Conde et al. (2000; 2004; 2007) made several in vitro studies on the excited-state properties and photostability of various MAAs in aqueous solution (see Table 1). The results showed picoseconds excited state lifetimes, very low fluorescence quantum yields (e.g., $\phi_F$ (porphyra 334) = 0.0016), very low triplet formation quantum yields (e.g., $\phi_T$ (porphyra 334) < 0.05), and very low photodegradation quantum yields (e.g., $\phi_R$ (porphyra 334) = 2 – 4 × 10^{-4}) for all of the MAAs studied. These results are consistent with a very fast internal conversion (IC) process as the main deactivation pathway of the excited states, which was directly quantified by photoacoustic calorimetry experiments showing that $\sim$ 97% of the absorbed photonic energy is promptly dissipated into the surrounding medium as heat (Conde et al., 2004).

A computational study by Sampedro (2011) using the CASPT2/\textit{CASSCF} protocol (Olivucci, 2005) and employing palythine as a model compound, confirmed these findings. The study indicates that the fast IC processes connecting the $S_2/S_1$ and $S_1/S_0$ states are due to the presence of two energetically accessible conical intersection points that can be reached by small geometrical changes in the atomic coordinates. It is now well established that conical intersections (a.k.a. molecular funnels or diabolic points) play a very important role in fast, non-radiative de-excitation transitions from excited electronic states to ground electronic state of molecules, particularly in many fundamental biological molecules, such as DNA/RNA, amino acids and peptides (Schermann, 2008). They enable effective coupling of the electronic degrees of freedom of the molecule to its phonon degrees of freedom, thereby facilitating radiationless decay by vibrational cooling to the ground state (in the process converting the absorbed high frequency UV photon into many low frequency infrared pho-
tons), which could make them examples of microscopic dissipative structuring of material in response to the impressed photon potential (Michaelian, 2016).

2.1.2 Ecological distribution

MAAs and mycosporines are cosmopolitan substances in “optical” habitats - planktonic, benthic and terrestrial; with the largest concentrations detected in environments exposed to high levels of solar irradiance (Castenholz and Garcia-Pichel, 2012 and references therein). They are now known to be the most common type of UV-absorbing natural substances, especially among aquatic organisms (Rastogi et al., 2010).

While mycosporines have been reported only in the kingdom Fungi (mycosporine-glycine and mycosporine-taurine are exceptions), MAAs are more extensively distributed among taxonomically diverse organisms (Karsten, 2008; Carreto and Carignan, 2011). These include: cyanobacteria; heterotrophic bacteria; dinoflagellates, diatoms and other protists; red algae; green algae; various marine animals, especially corals and their associated biota (for a database on the distribution of MAAs, see Sinha et al., 2007). They seem to be completely absent from terrestrial plants and animals, but are regularly found in terrestrial cyanobacteria (Garcia-Pichel and Castenholz, 1993) and terrestrial algae (Karsten et al., 2007).

An interesting discovery by Ingalls et al. (2010) reveals that MAAs represent a considerable portion of the organic matter bound to diatom frustules, accounting for 3-27% of the total carbon and 2-18% of total nitrogen content of the frustules. Previously established views held that MAAs have mainly an intracellular location in these organisms.

2.1.3 Biosynthesis

The cyclohexenone core of MAAs is derived from intermediates of two fundamental anabolic pathways; the shikimate pathway (Favre-Bonvin et al., 1987; Shick et al., 1999; Portwich and Garcia-Pichel, 2003) and the pentose phosphate pathway (Balskus and Walsh, 2010), with the shikimate pathway being the predominant route for UV-induced MAA biosynthesis (Pope et al., 2015).

In MAA/mycosporine biosynthesis both pathways converge at a point where their respective 6-membered cyclic intermediates with similar structures are converted to 4-deoxygadusol (Fig. 1), the common precursor of all MAAs and mycosporines, a reaction catalyzed by the key enzyme O-methyltransferase (Pope et al., 2015; D’Agostino et al., 2016).

These basic biochemical pathways lay at the heart of carbon metabolism, shared by all three domains of life; the shikimate pathway links carbohydrate catabolism to the biosynthesis of the aromatic amino acids and other aromatic biomolecules; similarly the pentose phosphate pathway uses glycolysis for the synthesis of pentose sugars, the nucleotide building blocks (Cohen, 2014). Thus, they are considered to have an ancient evolutionary origin, possibly even dating back to prebiotic times (Richards et al., 2006; Keller et al., 2014).

As mentioned in the previous section a very interesting trait of MAAs is that they are extremely prevalent natural compounds produced by a variety of taxonomically very distant
organisms from simple bacteria to algae and animals. A natural question arises: how can evolutionary so distant organisms share the same MAA encoding genes?

Several lines of evidence now suggest that the progenitor of the enzymatic machinery for MAA biosynthesis was probably a cyanobacterium or the cyanobacterial ancestor, while endosymbiotic events and prokaryote-to-eukaryote lateral gene transfer events during evolution account for their prevalence among all other biological taxa (Rozema et al., 2002; Waller et al., 2006; Starcevic et al., 2008; Singh et al., 2010; Singh et al., 2012).

Numerous in vitro experiments with manipulation of ambient UV light have demonstrated that wavelengths between 280-320 nm (UV-B) are generally the most effective inducers for the biosynthesis of MAAs, while UV-A and visible wavelengths have a lesser effect (Sinha et al., 2001; Rastogi and Incharoensakdi, 2014). Portwich and Garcia-Pichel (2000) proposed a certain reduced pterin molecule with a distinct absorption peak at 310 nm as the photoreceptor involved in the induction of cyanobacterial MAA biosynthesis.

### 2.1.4 Function: traditional view vs. thermodynamic view

Since their discovery in the 1960’s, authors have struggled to confer a single specific physiological function to MAAs. Although from the beginning a UV-photoprotective role seemed most conspicuous, largely because of their unique UV-dissipating traits and the fact that their production is stimulated by UV-B. Later, this theory faced serious challenges, for example, the failure to find a correlation between intracellular MAA accumulation and UV-resistance in certain coral zooxanthellae (Kinzie, 1993), the phytoplankton Phaeocystis antarctica (Karentz and Spero, 1995), the dinoflagellate Prorocentrum micans (Lesser, 1996), certain cyanobacterial strains (Quesada and Vincent, 1997), and the red alga Palmaria palmata (Karsten et al., 2003), etc.

As a response, many researchers in the field came up with their own suggestions for MAA physiological roles, sometimes very different from the sunscreen role, such as; osmotic regulation, antioxidants, nitrogen storage, accessory pigments, protection from desiccation, protection from thermal stress, reproductive functions in fungi and marine invertebrates, etc.; all of which have also been challenged or discredited (for reviews of the different theories of MAA functions and the challenges they face, see: Korbee et al., 2006; Oren and Gunde-Cimerman, 2007; Rosic and Dove, 2011).

From a traditional biological standpoint this apparent lack of a clear defining physiological function for these pigments looks extremely perplexing, especially when taking into account the extraordinary prevalence of these compounds in nature. Darwinian theory in its strictest traditional formulation, with evolution through natural selection operating only at the level of the individual, categorically dismisses this kind of phenomena; where an organism wastefully spends free energy and resources for the synthesis of metabolically expensive, nitrogen-containing compounds with no vital physiological function commensurate with their ubiquity and hence no, or little, benefit for its survival and reproduction. According to Darwinian theory, such a biosynthetic pathway, with little or no direct utility to the organism, should have been suppressed or completely eliminated through natural selection. However, exactly the opposite has happened in the course of evolution; MAA biosynthetic genes have not
only survived but have undergone extensive dissemination across numerous taxa through horizontal gene transfer.

The failure of Darwinian theory to find a niche for MAAs in its classical “struggle for survival” paradigm is a result of it not being soundly grounded in thermodynamics and the universal physical laws (for a discussion on this topic, see: Michaelian, 2011; 2012; 2016). From the perspective of non-equilibrium thermodynamics, a metaphysical “will to survive” does not exist, making the search for a particular physiological function of MAAs pointless. But MAAs do have a function and it is a thermodynamic function of energy dissipation, or, more generally, entropy production. This thermodynamic function can be readily inferred from their physicochemical properties related to photon dissipation described above. MAAs can be regarded as typical examples of microscopic dissipative structuring of matter for the sole purpose of entropy production through highly efficient dissipation of high-frequency UV photons into heat (Michaelian, 2016). This is the reason for their “coming into being” and tendency to proliferate over the surface of the Earth, as it is the fundamental reason for the origin and evolution of life on Earth, and, in fact, the reason for the ubiquity of organic pigments in the neighborhood of stars throughout the universe (Michaelian and Simeonov, 2017; Michaelian, 2016).

This biological irreversible process of photon dissipation that MAAs and other bio-pigments perform, then couples to a secondary abiotic irreversible process of water evaporation from surfaces through the heat it releases into its aquatic milieu (Michaelian, 2012). Evidence exist that the profusion of life and chromophoric dissolved organic matter (CDOM) in the sea-surface microlayer (SML) causes significant heating of the ocean surface fomenting evaporation (Morel, 1988; Kahru et al., 1993; Jones et al., 2005; Patara et al., 2012) and even the irreversible process of hurricane formation and steering (Gnanadesikan et al., 2010).

CDOM is the fraction of dissolved organic matter in water (DOM) that interacts with solar radiation (Nelson and Siegel, 2013). Light energy absorption by CDOM at the surface of the ocean usually exceeds that of phytoplankton pigments; 54 ± 15% of the total light absorption at 440 nm and > 70% of the total light absorption at 300 nm is due to CDOM (Siegel et al., 2002; Babin et al., 2003; Bricaud et al., 2010; Organelli et al., 2014). It is a complex and extremely variable mixture of organic pigments such as pheopigments (Bricaud et al., 2010), metal-free porphyrins (Röttgers and Koch, 2012), humic and fulvic acids (Carlson and Mayer, 1980; Galgani and Engel, 2016), aromatic amino acids (Yamashita and Tanoue, 2003) and MAAs (Whitehead and Vernet, 2000; Steinberg et al., 2004; Tilstone et al., 2010). While it was previously believed that CDOM in the open ocean is chiefly a byproduct of heterotrophic organisms recycling phytoplankton cell contents (Nelson et al., 1998), more recent observations (Romera-Castillo et al., 2010) suggest a large contribution from active plankton exudation.

Active secretion of MAAs into the surrounding water during surface blooms was demonstrated for the colonial cyanobacterium *Trichodesmium spp* (Subramaniam et al., 1999; Steinberg et al., 2004), for the dinoflagellate *Lingulodinium polyedrum* (Vernet and Whitehead, 1996; Whitehead and Vernet, 2000) and for the dinoflagellate *Prorocentrum micans* (Tilstone et al., 2010). Interestingly, Tilstone et al. (2010) found far greater MAA con-
centration in the sea-surface microlayer samples when compared to the near-surface (0-2 m), and sub-surface (0-110 m) samples. Whitehead and Vernet (2000) also concluded that free-floating MAAs contributed up to 10% of the UV absorption of the total DOM pool at 330 nm during the *L. polyedrum* bloom. This exudation of pigments by organisms into their environment would also seem to have little Darwinian advantage.

All of the evidence presented suffices to conclude, with some certainty, that MAAs join in function most of the other bio-pigments in nature which act as catalysts for the dissipation of photons into heat at Earth’s surface and the coupling of this heat to other abiotic entropy producing processes, such as; the water cycle, hurricanes, water and wind currents, etc.

### 2.2 Scytonemins

In 1849, Swiss botanist Carl Nägeli noted yellowish-brown cyanobacterial sheath coloration (Nägeli, 1849), and in 1877 coined the name “scytonemin” for the color-producing pigment (Nägeli and Schwenderer, 1877). Although occasionally mentioned in scientific papers during the twentieth century, scytonemin was not isolated until 1991 when Garcia-Pichel and Castenholz (1991) first made a more extensive study of the compound. Proteau et al. (1993) elucidated the chemical structure of scytonemin, which proved to be a completely novel indolic-phenolic dimeric structure unique among all hitherto known natural organic substances. The carbon skeleton of this novel eight-ring homodimeric molecule was given the trivial name “the scytoneman skeleton” (Proteau et al., 1993). Already in 1994, another scytoneman-type molecule was isolated from the cyanobacterium *Nostoc commune*, and termed “nostodione A” (Kobayashi et al., 1994). Thus far, four additional substances with a scytoneman-type molecular structure, or a structure derived from it, have been isolated from cyanobacteria: dimethoxyscytonemin, tetramethoxyscytonemin, scytonine (Bultel-Poncé et al., 2004) and scytonemin-imine (Grant and Louda, 2013); for which, in this review, we use the colloquial terms “scytonemins” or “scytoneman pigments”.

#### 2.2.1 Physicochemical properties

Scytonemin (Fig. 3), the representative and most common member of this yet poorly-explored family of aromatic indole alkaloids, is a relatively small molecule (544 u) built from two identical condensation products of tryptophanyl- and tyrosyl-derived subunits linked through a carbon-carbon bond (Proteau et al., 1993). Its IUPAC name is (3E,3’E)-3,3’-Bis(4-hydroxybenzylidene)-1,1’-bicyclopenta[b]indole-2,2’(3H,3’H)-dione.

Depending on the redox conditions it can exist in two inter-convertible forms: a predominant oxidized yellowish-brown form which is insoluble in water and only fairly soluble in organic solvents, such as pyridine and tetrahydrofuran, and a reduced form (Fig. 3) with bright red color that is slightly more soluble in organic solvents (Garcia-Pichel and Castenholz, 1991; Proteau et al., 1993). Dimethoxy- and tetramethoxyscytonemin can be considered as derivatives of reduced scytonemin, where one or both of the ethenyl groups in the molecule have been saturated by two or four methoxy groups, respectively (Bultel-Poncé et al., 2004; Varnali and Edwards, 2010). Another moderate degree of modification of
the parent scytoneman skeleton can also be seen in scytonemin-3a-imine (a.k.a. scytonemin-imine), where the C-3a atom of scytonemin has been appended with a 2-imino-propyl radical (Grant and Louda, 2013).

Only the structure of scytonine deviates substantially from the dimeric scytoneman skeleton, due to the loss of one para-substituted phenol group and ring openings of both cyclopentenones where successive methoxylation and secondary cyclizations take place (Bultel-Poncé et al., 2004).

A full in-depth photophysical and photochemical characterization of scytonemins has yet to be attained; thus far only their elemental spectroscopic properties are known. Scytonemin absorbs very strongly and broadly across the UV-C-UV-B-UV-A-violet-blue spectral region (see Fig. 2 and Fig. 4), with in vivo $\lambda_{\text{max}}$ at 370 nm and in vitro (tetrahydrofuran) $\lambda_{\text{max}}$ at 386 and 252 nm, with smaller peaks at 212, 278 and 300 nm (Garcia-Pichel and Castenholz, 1991; Garcia-Pichel et al., 1992; Sinha et al., 1999). Its observed long term persistence in cyanobacterial biocrusts or dried mats exposed to intense solar radiation might be an indication of exceptionally high photostability (Garcia-Pichel et al., 1992; Brenowitz and Castenholz, 1997; Fleming and Castenholz, 2007; Fulton et al., 2012; Lepot et al., 2014).

Reduced scytonemin has a similar spectroscopic profile, with in vitro (tetrahydrofuran) $\lambda_{\text{max}}$ (nm) and $\varepsilon$ ($M^{-1}cm^{-1}$) values: 246 (30000), 276 (14000), 314 (15000), 378 (22000), 474 (14000) and 572 (broad shoulder 7600) (Varnali and Edwards, 2014). A comparable absorption spectrum is also exhibited by scytonemin-imine, the mahogany-colored, polar derivative of scytonemin, with slightly different $\lambda_{\text{max}}$ values when measured in acetone (237, 366, 437 and 564 nm) and in ethanol (248, 305, 364, 440 and 553 nm) (Grant and Louda, 2013). Contrary to these three scytoneman-type molecules, the methoxylated derivatives and scytonine do not absorb strongly in the UV-A region but have very high absorbances in the UV-C region with in vitro (methanol) $\lambda_{\text{max}}$ (nm) and $\varepsilon$ ($M^{-1}cm^{-1}$) values for dimethoxyscytonemin: 215 (60354), 316 (18143) and 422 (23015); for tetramethoxyscytonemin: 212 (35928).
and 562 (5944); and for scytonine: 207 (38948), 225 (37054) and 270 (22484) (Bultel-Poncé et al., 2004).

Concerning the monomeric scytoneman-type molecules nostodione A and prenostodione, isolated from natural cyanobacterial blooms, it remains debatable whether they are genuine cyanobacterial pigments or just intermediates in the biosynthesis of scytonemin (Ploutno and Carmeli, 2001; Soule et al., 2009a).

2.2.2 Ecological distribution

Unlike MAAs, scytonemins are exclusively cyanobacterial sheath pigments (Pathak et al., 2016). All phylogenetic lines of sheathed cyanobacteria contain scytonemins (Proteau et al., 1993), notably strains of the genera *Nostoc*, *Calothrix*, *Scytonema*, *Rivularia*, *Chlorogloeopsis*, *Lyngbya*, *Hyella*, etc. (Sinha and Häder, 2008); as well as cyanolichens of the genera *Peltula*, *Collema* and *Gonohymenia* (Büdel et al., 1997).

The mucilaginous extracellular sheath (matrix) consists of heteroglycans, peptides, proteins, DNA and different secondary metabolites (Pereira et al., 2009), where scytonemins are usually deposited in the outer layers, giving the sheath its distinctive dark yellow to brown color (Ehling-Schulz et al., 1997; Ehling-Schulz and Scherer, 1999). Up to 5% of the dry weight of cultured scytonemin-synthesizing cyanobacteria is due to the pigment, but in natural assemblages this value can be even higher (Karsten et al., 1998). Curiously, Abed et al. (2010) reported two to six times higher concentrations of scytonemin than chlorophyll *a* in cyanobacterial cryptobiotic soil crusts in the Oman Desert.

Scytonemin-producing cyanobacteria typically inhabit highly insolated terrestrial, fresh-
water and coastal environments such as deserts, exposed rocks, cliffs, marine intertidal flats, shallow oligotrophic fresh waters, hot springs, etc. (Castenholz and Garcia-Pichel, 2012 and references therein). In microbial mat communities, especially the extremophilic terrestrial and aquatic colonies, these cyanobacteria occupy the uppermost sunlit layers (Balskus et al., 2011). Scytonemin-imine, for example, was isolated from samples of natural *Scytonema hoffmani* mats growing under high to intense (300-2000 µmol quanta m$^{-2}$s$^{-1}$) photon flux density (Grant and Louda, 2013). The methoxyscytonemins and scytonine were isolated alongside scytonemin from colonies of *Scytonema sp.* growing on exposed granite at the Mitaraka inselberg in French Guyana, a region subjected to intense UVR-insolation (Bultel-Poncé et al., 2004).

### 2.2.3 Biosynthesis

The biochemistry and genetics of cyanobacterial scytonemin biosynthesis has extensively been investigated by Soule et al. (2007; 2009a; 2009b), Balskus and Walsh (2008; 2009; 2011) and Sorrels et al. (2009). They have confirmed the assumption by Proteau et al. (1993), the discoverers of the scytonemin structure, that the scytoneman molecular scaffold is actually a condensation product of the aromatic amino acids tryptophan and tyrosine. Michaelian (2011) and Michaelian and Simeonov (2015) have hypothesized that these were the first amino acids to enter into a photon-dissipation-driven association with nucleic acids in the prebiotic world, a scenario backed by their high conservation inside the DNA-binding sites of photolyase enzymes (Kim et al., 1992; Weber, 2005); a phylogenetically ancient family of enzymes, common to all three domains of life (Selby and Sancar, 2006) and even found in viruses (Srinivasan et al., 2001). Not only do these amino acids absorb in the UV themselves (Michaelian and Simeonov, 2015 and references therein), but they also serve as biosynthetic precursors for most known aromatic UV-absorbing bio-pigments, including: anthocyanins, flavonoids and polyphenols in plants, melanins in heterotrophic organisms, scytonemins in cyanobacteria, etc. (Knaggs, 2003).

Eight of the genes that make up the 18-gene scytonemin biosynthesis cluster code for shikimate pathway enzymes for the biosynthesis of tryptophan and tyrosine, while the functions of the rest remain unresolved but are suspected to be involved in the coupling of the tryptophan- and tyrosine-derived precursors for the formation of the scytoneman skeleton (Ferreira and Garcia-Pichel, 2016). The expression of the whole gene cluster has been shown to be elicited by exposure to UV-A and UV-B light (Sorrels et al., 2009; Rastogi and Incharoensakdi, 2014).

Sorrels et al. (2009) proposed an ancient evolutionary origin for the scytonemin biosynthetic pathway based on the combination of the fact that this gene cluster is highly conserved among evolutionary diverse strains of cyanobacteria (Soule et al., 2007; 2009a), and their own phylogenetic analyses implying that the cluster is under a purifying selection pressure. Intriguingly, Soule et al. (2009a) observed scytonemin biosynthetic genes even in some cyanobacterial strains incapable of producing the pigment (e.g., *Anabaena* and *Nodularia*), and interpreted this as a case of relic genetic information.
2.2.4 Function: traditional view vs. thermodynamic view

Similarly to MAAs, the Darwinian point of view can only describe scytonemin as an efficient protective biomolecule designed to filter out supposedly damaging high frequency UV radiation while at the same time allowing the transmittance of wavelengths necessary for photosynthesis (Ekebergh et al., 2015).

Within the framework of this traditional “struggle for survival” viewpoint, the majority of authors define scytonemins as an adaptive mechanism of extremophilic cyanobacteria that colonize harsh, inhospitable habitats experiencing high doses of UVR-insolation (Ehling-Schulz et al., 1997; Wynn-Williams et al., 1999; Hunsucker et al., 2001; Sinha and Hader, 2008; Rastogi et al., 2014).

Among the evidence for the accredited photoprotective role is the discovery that up to 90% of incident UV photons are prevented from entering sheathed, scytonemin-producing cyanobacterial cells, thus accomplishing significant reduction in chlorophyll a photobleaching and maintaining photosynthetic efficiency (Garcia-Pichel and Castenholz, 1991; Garcia-Pichel et al., 1992). Other authors, in addition to the sunscreen role, ascribe supplementary defensive roles to scytonemin such as protection from oxidative, osmotic, heat and desiccation stress (Dillon et al., 2002; Matsui et al., 2012).

Furthermore, scytonemin’s superior UV-C-absorbing capabilities in vivo, experimentally proven by treating cyanobacterial colonies with 0.5-1.0 Wm$^{-2}$ UV-C radiation added to natural solar irradiance (Dillon and Castenholz, 1999), has led many authors to consider modern cyanobacterial production of scytonemins as a relic UV-protection mechanism from the pre-Great Oxygenation Event period (Garcia-Pichel, 1998; Hader et al., 2003). Indeed, Raman spectral biosignatures of scytonemins, carotenoids and porphyrins were unambiguously identified in $\sim$3.5 Ga old relict fossilized sedimentary geological specimens (Edwards et al., 2007; Pullan et al., 2008). Extracellular pigments, presumably scytonemins, also seem to occur in $\sim$2.0 Ga old cyanobacterial microfossils preserved in silicified stromatolites that grew in tidal or shallow subtidal waters (Hofmann, 1976; Golubic and Hofmann, 1976; Golubic and Abed, 2010).

Although it is beyond doubt that the efficient UV absorption and dissipation properties of the scytoneman pigments provide, to some extent, a beneficiary effect for the survival of sheathed cyanobacterial cells, the stance that this is the primary reason for the biological production of these pigments may be erroneous. Here are few examples of serious challenges and inconsistencies that the photoprotection paradigm faces:

1. Inability to explain the strong visible absorption bands of scytonemin-imine, where photosynthetic pigments absorb. The question is raised by Grant and Louda (2013): “The absorption spectrum ($\lambda_{\text{max}} = 237, 366, 437, 564$ nm in vitro), extending from the ultraviolet (UVB & UVA) into the blue and green of the visible, appears to indicate a photoprotective role beyond shielding only UVR. That is, going on the premise that evolution generates and retains only advantageous secondary metabolites, then what is the role of the visible bands in this case?”

2. Inability to explain the production of the strongly UV-C/UV-B-absorbing methoxyscy-
tonemins and scytonine, in spite of the absence of UV-C wavelengths and the low intensity of UV-B in today’s surface solar spectrum. The question is raised by Varnali and Edwards (2010): “The realization that scytonemin is the parent molecule of perhaps a whole family of related molecules is important in that an analytical challenge is generated to detect these family members in admixture and in the presence of each other naturally, and also the question is raised about the role of these molecules in the survival strategy processes involving scytonemin; what subtle changes to the radiation absorption process require molecular modification of what apparently is already a highly successful radiation protectant, especially when the molecular syntheses are accomplished in energy-poor situations?”

3. Inability to explain why many species of cyanobacteria do not synthesize scytonemins nor MAAs but, nevertheless, successfully cope with UV-induced cellular damage by employing only metabolic repair mechanisms (Quesada and Vincent, 1997; Castenholz and Garcia-Pichel, 2000).

4. Soule et al. (2007) developed scytoneminless mutant of the cyanobacterium Nostoc punctiforme which proved to have indistinguishable growth rate from the wild type after both were subjected to UV-A irradiation. The conclusion of the authors was that other photoprotective mechanisms can fully accommodate the absence of scytonemin in the mutant.

In addition, very efficient absorption and dissipation of high-energy photons is not a prerequisite for photoprotection, but it is for dynamical dissipative structuring of material under an external generalized chemical potential. Nature has a simpler way of creating photoprotective molecules, if this was really the intention, by making them either highly reflective or transparent to UV wavelengths (Michaelian, 2016).

These problems and paradoxes, generated when trying to explain scytonemins from within the Darwinian photoprotection paradigm, can be resolved by employing established non-equilibrium thermodynamic principles. In this context, we will first address the questions raised by Grant and Louda (2013) and Varnali and Edwards (2010), and then, based on all the evidence presented, we will assign a thermodynamic dissipative role to scytonemins.

The seemingly paradoxical absorption spectra of scytonemin-imine, the methoxyscytonemins and scytonine, which extend outside of the photoprotectively-relevant part of the spectrum, make sense only when these bio-pigments are understood as microscopic dissipative structures obeying non-equilibrium thermodynamic directives related to increasing the global solar photon dissipation rate (Michaelian, 2013; Michaelian and Simeonov, 2015; Michaelian, 2016). Under these directives, one of the several ways to increase the global solar photon dissipation rate is by evolving (inventing) novel molecular structures (pigments) that cover ever more completely the prevailing surface solar spectrum (see Michaelian and Simeonov, 2015). This is precisely what is observed in the absorption spectra of the different scytoneman pigments. The strong visible absorption peaks of scytonemin-imine at 437 nm (violet) and 564 nm (green/yellow), of tetramethoxyscytonemin at 562 nm (green/yellow), of dimethoxyscytonemin at 422 nm (violet); and the strong near-UV-C/UV-B absorption
peaks of scytonine (270 nm) and dimethoxyscytonemin (316 nm) is exactly where the photosynthetic pigments do not peak in absorption (see, for example, Rowan, 1989). It is because of this rich assortment of diverse pigment molecules with complementary absorption bands that cyanobacterial biofilms, mats and soil crusts in nature tend to have high absorptivities, low albedos and appear almost black in color (Ustin et al., 2009).

This fact leads us to an important conclusion on the thermodynamic function of the scytoneman pigments. We believe that it is most reasonable to consider the photon-dissipation role of scytonemins as the terrestrial analogue of the function that MAAs perform in the open aquatic environment. This assertion may be justified on their hydrophobic character and their inextricable connection to the extracellular polymeric substances (EPSs) of the cyanobacterial sheaths. Ekebergh et al. (2015) have shown that scytonemins have the greatest photostability in vivo, where they are embedded in their natural extracellular matrix milieu. These extracellular polymeric substances may therefore be playing the role of providing the dissipative medium required to disperse the excess vibrational energy after photon excitation of the pigment, bringing the system rapidly to the ground state.

In wet terrestrial regions of the planet, the thermodynamic role of photon dissipation coupled to the water cycle is performed mainly by the plant cover, but in arid and semi-arid lands, where vegetation is severely restricted, this function is allotted to microscopic assemblages of cyanobacteria, heterotrophic bacteria, algae and fungi known as biological soil crusts or biocrusts (Evans and Johansen, 1999; Belnap and Lange, 2001). It is theorized that these types of microbial communities represented life’s pioneering on dry land and were the dominant ecosystem on the continents up until the advent of land plants and animals in the Early Devonian (Beraldi-Campesi et al., 2014).

Michaelian (2013) postulated: “The most important thermodynamic work performed by life today is the dissipation of the solar photon flux into heat through organic pigments in water. From this thermodynamic perspective, biological evolution is thus just the dispersal of organic pigments and water throughout Earth’s surface... On Earth, organic molecules are found only in association with water. As described above, this is most likely related to the efficiency of organic pigments dissipating solar photons using the high frequency water vibrational modes to facilitate their de-excitation. Without water they are poor photon dissipaters and easily destroyed by photochemical reactions. This is probably the primordial reason for the association of life with water.”

In the context of this citation, we emphasize the fact that cyanobacteria isolated from dry regions display very high capacity to excrete large amounts of EPSs (Huang et al., 1998; Hu et al., 2003; Roeselers et al., 2007; Rossi et al., 2012), which are the main constituent of the biofilm matrix and together with microbial filaments play a key structural role in forming the biocrusts (Mager and Thomas, 2010; Karunakaran et al., 2011). The unique hydrophilic/hydrophobic nature of the EPSs enables highly efficient water capture and water storage within the biocrust by allowing the creation of moistened microenvironments where water dynamics is intricately regulated (Colica et al., 2014 and references therein). Hence, crust-covered soils are very hygroscopic and always exhibit higher water content compared to bare neighboring surfaces (Rossi and Phillips, 2015). This phenomenon is exactly what
we have postulated earlier, life’s fundamental role of “dispersing organic pigments and water over Earth’s entire surface” (Michaelian, 2013).

A very conspicuous analogy between these terrestrial macroscopic and microscopic photon-dissipating biological “carpets” can be drawn. In the same manner as ecological succession of plant coverage leads to old climax forests with higher pigment content and lower albedos (Pokorny et al., 2010; Maes et al., 2011), ecological succession in biocrusts leads to increase in biomass of the late-stage scytonemin-producing cyanobacteria, and consequently accumulation of scytonemins in the matrix, an effect macroscopically observed as darkening of the biocrusted soil (i.e. decrease in albedo) (Couradeau et al., 2016). During dry periods in deserts when water availability is very limited, the heat generated from scytonemin’s photon dissipation is expected to go predominantly into sensible heat of the biocrusts instead of into the latent heat of vaporization of water, and this is exactly what Couradeau et al. (2016) found when they measured $\sim 10^\circ$C higher temperature of biocrust-covered, dark soils in comparison to bare soils.
3 Discussion

In a previous work (Michaelian and Simeonov, 2015) we posited five basic tendencies that organic pigment evolution on Earth would have followed: (1) increases in the photon absorption cross section with respect to the pigment physical size, (2) decreases in the electronic excited state lifetimes of the pigments, (3) quenching of the radiative de-excitation channels (e.g., fluorescence), (4) greater coverage of the surface solar spectrum, and (5) pigment proliferation and dispersion over an ever greater surface area of Earth.

To examine whether these five tendencies are satisfied with the evolutionary invention of MAAs and scytonemins we compare their properties to those of the aromatic amino acids (AAAs) (see Table 1).

Our reason for choosing the AAAs is twofold; (1) they are considered to be among the earliest chromophoric organic molecules used by life with a prebiotic origin (a subject discussed earlier in the text, and in Michaelian (2011) and Michaelian and Simeonov (2015) in greater detail), and (2) since both MAAs and scytonemins are derived from intermediates of the shikimate pathway for AAA biosynthesis they most likely appeared later in evolution compared to the AAAs, probably when the biosynthetic machinery for the synthesis of the AAAs was already robust; an event that most likely long predated 3.4 Ga, considering that Busch et al. (2016) demonstrated that the ancestral tryptophan synthase of the last universal common ancestor (LUCA) was already a highly sophisticated enzyme at 3.4 Ga. This reasoning is also corroborated by the previously mentioned (see Sect. 2.2.4) identification of Raman spectral biosignatures of scytonemin in ∼3.5 Ga old relict fossilized sedimentary geological specimens (Edwards et al., 2007; Pullan et al., 2008).

Based on all the data presented and discussed in Sect. 2, we can state with a high degree of certainty that the fourth and fifth requirements are satisfied with the evolutionary inventions of MAAs and scytonemins.

For the first to third requirements, in addition to the previously discussed material, we offer data presented in Table 1. The data has been extracted from the available literature and as of 2017 is exhaustive. All of the compounds listed are representative members of their respective chemical groups. Gadusol is used instead of the more relevant compound 4-deoxygadusol because of lack of available data on 4-deoxygadusol and because of their chemical relatedness with similar spectroscopic properties (Losantos et al., 2015a, 2015b). The $\lambda_{max}$ and $\varepsilon$ values of gadusol in water are pH-dependent: 268 nm at pH $< 7$ and 296 nm at pH $\geq 7$ (Losantos et al., 2015a), and in Table 1 we use the values for acidic pH, having in mind that the Archean seawater was probably slightly acidic with pH $\sim 6.5$ (Holland, 2003). All absorption peaks and attenuation coefficients below about 220 nm, we believe, are due to the ionization of the molecules, a process which could destroy them. Photon dissipation is not through a conical intersection at these very short wavelengths and this is why they are omitted from Table 1 and Fig. 5.

It is our hope that future experiments and studies into the nature and properties of these bio-pigments will help complete all of the data missing from the table. However, even with the limited data available and presented in this article, a trend compatible with our conjecture is evident.
Table 1: Comparison between the photophysical properties of the aromatic amino acids and representative compounds of the major classes of cyanobacterial UV-absorbing pigments

| UV-absorbing bio-pigments | λ<sub>max</sub> (nm) | ε (M<sup>-1</sup>cm<sup>-1</sup>) | Electronic excited state lifetime (ns) | Fluorescence quantum yield (φ<sub>F</sub>) |
|---------------------------|---------------------|--------------------------------|--------------------------------------|----------------------------------------|
| **Aromatic amino acids**  |                     |                                |                                      |                                        |
| Phenylalanine (a)         | 257                 | 195                            | 7.5                                  | 0.024                                  |
| Tyrosine (a)              | 274                 | 1405                           | 2.5                                  | 0.14                                   |
| Tryptophan (a)            | 278                 | 5579                           | 3.03                                 | 0.13                                   |
| **Mycosporines and MAAs** |                     |                                |                                      |                                        |
| Gadusol (b)               | 260                 | 12400                          |                                      | non-fluorescent                        |
| Mycosporine-γ-aminobutyric acid (c) | 310 | 28900 | -                              | -                                      |
| Mycosporine-glutamic acid (c) | 311 | 20900 | -                              | -                                      |
| Palythine (b, c)          | 320                 | 36200                          |                                      | non-fluorescent                        |
| Shinorine (b)             | 333                 | 44700                          | 0.35                                 | 0.002                                  |
| Porphyra-334 (b)          | 334                 | 42900                          | 0.4                                  | 0.0016                                 |
| Palythene (c)             | 360                 | 50000                          |                                      | -                                      |
| **Scytonemins**           |                     |                                |                                      |                                        |
| Scytonemin (d)            | 252, 278, 300, 384 |                                |                                      |                                        |
| Reduced Scytonemin (d)    | 246, 276, 314, 378, 474, 572 | 30000, 14000, 15000, 22000, 14000, 7600 | -                                    | -                                      |
| Scytonemin-imine (e)      | 237, 366, 437, 564 | -                              |                                      | -                                      |
| Dimethoxyscytonemin (d)   | 316, 422           | 18143, 23015                   |                                      | -                                      |
| Tetramethoxyscytonemin (d) | 562 | 5944 | -                              | -                                      |
| Scytonine (d)             | 225, 270           | 47854, 22484                   |                                      | -                                      |
| **Other poorly characterized cyanobacterial UV-absorbing pigments** |                     |                                |                                      |                                        |
| Gloeocapsin (f)           | 392                 | -                              |                                      | -                                      |
| Microrythysteopterine (g)  | ~ 275, ~ 350       | 10000, 3500                    |                                      | -                                      |

a)Berezin and Achilefu (2010); b)Losantos et al. (2015a); c)Wada et al. (2015); d)Varnali and Edwards (2014); e)Trent and Lewis (2013); f)Steeve et al. (2014); g)Lifshits et al. (2016).
Figure 5: The expected Earth surface solar spectrum at the given dates since present (Michaelian and Simeonov, 2015) and the maximum absorption ($\lambda_{max}$) of the mycosporine and scytoneman pigments and their aromatic amino acid precursors. The precursors have strong absorptions only in the UV-C (230-280 nm) while scytonemins absorb strongly across the UV-C, UV-B, UV-A, violet and blue regions, and mycosporines and MAAs usually have strong absorption in the UV-B and UV-A regions. Neither scytonemins nor MAAs peak strongly in the UV-B region from $\sim$ 280-310 nm because aldehydes (CH$_2$O and CH$_3$CHO) produced by UV-C light on common volcanic gases such as H$_2$S, H$_2$O and CO$_2$, were absorbing strongly in this gap. This gap was later covered by O$_2$ and O$_3$ absorption after the Great Oxygenation Event at $\sim$ 2.3 Ga. The age of the given spectrum and the corresponding estimated integrated energy fluxes midday at the equator are listed.
Another conjecture made in Michaelian and Simeonov (2015) states that the surface solar spectrum wavelength region from approximately 280 to 310 nm has never reached the surface of the Earth during its entire geologic history; because during the Hadean and Archean eons these wavelengths were probably absorbed by atmospheric aldehydes (formaldehyde and acetaldehyde) (Sagan, 1973), and from the end of the Archean onwards gradual accumulation of oxygen and stratospheric ozone was responsible for their attenuation (Matsumi and Kawasaki, 2003; Stanley, 2008). In this earlier paper we also demonstrated how numerous fundamental molecules of life, common to all three domains of life, have strong absorbances across the UV-C, UV-B and UV-A regions except in this interval, which we used as an argument in favor of the thermodynamic dissipation theory of the origin and evolution of life (Michaelian, 2009; 2011; Michaelian, 2012).

Here we demonstrate how this “rule” can also be applied to the cyanobacterial UV-absorbing pigments scytonemins and MAAs, which can be considered as evolutionary successors to the primordial pigments of life, specifically the AAAs. From the information presented in Table 1, Fig. 5, and Sect. 2, it is obvious that none of the compounds discovered so far, from both pigment groups, peak strongly in absorption inside this wavelength interval, which is consistent with our conjecture.

The absorption spectrum of scytonemin alone (Fig. 4) has a very interesting shape which seems to adhere perfectly to this pattern. Although it is continuous from \( \sim 220 \) to \( \sim 700 \) nm, there is a dip in the \( \sim 275 \) to \( \sim 325 \) nm interval, and two large maxima at \( \sim 250 \) nm and \( \sim 380 \) nm. This is exactly the kind of shape that would be expected if the selective force for the evolution of this pigment was our proposed Archean surface solar spectrum (Michaelian and Simeonov, 2015). Combining this crucial point with the previously discussed facts on scytonemin, it is tempting to speculate that this pigment had a key role in photon dissipation during the Archean, being capable of dissipating almost the entire Archean surface solar spectrum. The evolutionary invention of scytonemin’s derivatives, as well as the mycosporines, the MAAs and still many other extinct and extant biological pigments, most likely resulted from the necessity to complement scytonemin’s absorption with pigments that absorbed wavelengths reaching Earth’s surface but were poorly absorbed by scytonemin itself. This kind of complementary spectral relationship between scytonemin and the MAAs has been well documented by several authors (e.g., Ehling-Schulz and Scherer, 1999; Ferroni et al., 2010; Castenholz and Garcia-Pichel, 2012) and is illustrated in Fig. 2.
4 Conclusions

The available data on the ubiquity of pigments covering the region from the UV-C to the infrared, many exuded by the organisms that produce them into the environment, make it increasingly difficult to assign to them a protective or antenna role within the Darwinian paradigm of the optimization of photosynthesis in benefit of the organism. We believe that sense can only be made of this by shifting the paradigm from one of “photoprotection” of the organism to the thermodynamic optimization of photon dissipation.

A number of contemporary pigment lines, most notably scytonemins and the mycosporine-like amino acids, appear to harbor relics of ancient biosynthetic production routes based on the most ancient of the amino acids, the aromatics. The aromatic amino acids have known affinities to their RNA anticodons (Majerfeld and Yarus, 2005; Yarus et al., 2009) and were perhaps the first antenna pigments for photon dissipation in the UV-C at the beginnings of life (Michaelian, 2011).

These pigment lines absorb and dissipate rapidly in the UV-C as well as the UV-B, UV-A and the visible. Some of these pigments are exuded into the environment which excludes the possibility of assigning them a role in photoprotection. Their strong absorption and dissipation in regions out of the photosynthetically active radiation (PAR) has been perplexing to perspectives within the Darwinian paradigm since these pigments appear to have little utility to the organisms themselves. In fact, they absorb exactly where the photosynthetic pigments do not (and where water does not) and appear to have complete coverage of the Archean to present day Earth surface solar spectra.

It should be emphasized that our current knowledge of the diversity of cyanobacterial, algal and plant pigments and the thermodynamic function they perform is incomplete. For example, there are several indications of even richer diversity of UV-absorbing pigments in cyanobacteria than those hitherto characterized and classified into the two groups, mycosporines and scytonemins. The chemical structure and other elemental properties of one of these poorly investigated pigments, named gloeocapsin, have yet to be determined, but initial results suggest that it is chemically unrelated to both MAAs and scytonemins (Storme et al., 2015). Still other chemically distinct UV-absorbing cyanobacterial pigments, with a unique pterin structure, have been reported elsewhere (Matsunaga et al., 1993; Lifshits et al., 2016). The wavelengths of maximum absorption of these two ill-defined groups of cyanobacterial pigments are listed in Table 1 and are plotted in Fig. 5. As with the mycosporines and the scytonemins, their absorption properties are consistent with the optimization of dissipation of the prevailing photon spectrum at Earth’s surface.

Taken as a whole, these data seem to indicate that, rather than photosynthesis being optimized under a Darwinian “survival of the fittest” paradigm, that the origin and evolution of life is driven by photon dissipation with the net effect of covering Earth’s entire surface with pigments and water, reducing the albedo and the black-body temperature at which Earth radiates into space. It is our hope that this article will incite further investigation into the proposition that photon dissipation efficacy has been the fundamental driver of biological evolution on Earth.
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