

Reply to Lars Olof Björn's comment on "Fundamental molecules of life are pigments which arose and co-evolved as a response to the thermodynamic imperative of dissipating the prevailing solar spectrum" by Michaelian and Simeonov (2015)

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Abstract. Lars Björn doubts our assertion that 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 global solar photon dissipation. Björn bases his critique on the fact that the albedo of non-biological material can sometimes be lower than that of biological material and concludes that such examples counter our assertion. Our reply to Björn, however, is that albedo (reflection) is only one factor involved in the entropy production through photon dissipation occurring in the interaction of light with material. The other contributions to entropy production, which were listed in our article, are (1) the shift towards the infrared of the emitted spectrum (including a wavelength-dependent emissivity), (2) the diffuse reflection and emission of light into a greater outgoing solid angle, and (3) the heat of photon dissipation inducing evapotranspiration in the pigmented leaf, thereby coupling to the abiotic dissipative processes of the water cycle, which, besides shifting the emitted spectrum even further towards the infrared, promotes pigment production over the entire Earth surface. His analysis, therefore, does not provide a legitimate reason for doubting our assertion that life and evolution are driven by photon dissipation. We remain emphatic in our assertion that the fundamental molecules of life were originally dissipatively structured UV-C pigments arising in response to the thermodynamic

imperative of dissipating the prevailing Archean solar spectrum.

In the following, we respond to Björn's comment using the same section headings.

1 Introduction: do living systems reduce the albedo of Earth?

Contrary to Björn's examples, in general, living organisms do, in fact, reduce the albedo with respect to regions devoid of life. For example, the visible albedo of deciduous forests is 0.15 to 0.18, and that of coniferous forests is 0.09 to 0.15, while that of sandy deserts is about 0.30 (Barry and Chorley, 2009), and that of rocky deserts (Gobi) is about 0.21 (Wang et al., 1998). This is also true at wavelengths beyond the red edge (\sim 700 nm). For example, at these longer wavelengths, forest albedo increases to about 0.3 (Coakley, 2003), while sand and rocky desert albedo increases to about 0.50 (Varotsos et al., 2014; Coakley, 2003).

More importantly, however, as emphasized in our article, determining entropy production due to light interacting with material entails not only knowing reflection, but also wavelength-dependent absorptivity and emissivity. In Michaelian and Cano (2022) we show that, given a particular (non-zero) average albedo and emissivity, greater entropy production occurs when absorption is strongest at short wavelengths and emission is strongest at long wavelengths. Maximum entropy production occurs when the material acts as if it were a black body, i.e., with maximal absorptivity (zero albedo) and maximal emissivity (100%) across all wavelengths. Detailed calculations show that biological material more closely approaches a black body than nonbiological material and produces more entropy through photon dissipation (Michaelian and Cano, 2022).

Our objection to Björn's critique is thus that it is based on the assumption that albedo is the only important factor relevant to photon dissipation in the light-material interaction. Björn states, "Thus, it appears that if Michaelian and Simeonov are correct, one would expect organisms (in particular phototrophic organisms, or the biosphere) to be less reflecting and more absorbing than dead matter". But one should not de facto "expect" this since, as we mentioned even in the abstract of our original article (Michaelian and Simeonov, 2015), other factors important to entropy production are (1) the redshifting of the absorbed energy in the pigments (including wavelength-dependent emissivity); (2) dispersion of the emitted, reflected, and transmitted photon beams into a larger outgoing solid angle; and (3) the coupling of photon dissipation in pigments to other abiotic entropy-producing processes, such as the water cycle (Michaelian, 2012a, b). The water cycle (i) further redshifts the incoming spectrum; (ii) reduces the difference between day and night temperatures, providing emission into a greater 4π solid angle; and (iii) allows proliferation of organic pigments over the entire surface of Earth, all of which increase entropy production.

The importance of these other factors can be seen when performing a calculation of the global entropy production of Earth. In Michaelian (2012b) we evaluate this by determining the difference in the entropy of the incoming and outgoing photon beams and compare this to Earth's neighboring planets Venus and Mars. We find that Earth's entropy production per unit area, after normalizing for distance from the Sun, is significantly greater than that of either neighbor, and we conclude that this is most probably due to the presence of life on Earth. In support of this conclusion, Kleidon et al. (2000) compare surface temperatures and amount of atmospheric water vapor for a simulated Earth with and without life. They find an 8 °C average lower temperature and 3 times the amount of water vapor in the atmosphere for the simulation including life. The lower temperature and greater amount of water vapor imply (see below) greater entropy production for an Earth with life.

2 Ancient life

The thermodynamic dissipation theory of the origin of life suggests that the fundamental molecules of life (nucleic acids, amino acids, fatty acids, cofactors, etc.) were originally UV-C pigments dissipatively structured on the ocean surface from common precursor molecules such as HCN, cyanogen, CO₂, and water under the UV-C photon flux (between 210 and 285 nm) arriving at Earth's surface during the Archean (Michaelian, 2011, 2017, 2021; Hernández and Michaelian, 2022). This wavelength region has sufficient energy per photon to transform carbon covalent (and double covalent) bonds but not enough energy to ionize these molecules and thereby destroy them. The best geochemical evidence presently available suggests that this light would have been present on Earth's surface from before the origin of life (at ~ 3.9 Ga) and for at least 1000 million years (and perhaps even for 1500 million years; Meixnerová et al., 2021) until organisms evolved oxygenic photosynthesis and saturated available oxygen sinks (Sagan, 1973; French et al., 2015; Meixnerová et al., 2021), leading to an ozone layer. We thus consider ozone as a biology-procured pigment dissipating the UV-C region. Also around this time, biosynthetic pathways evolved enough for life to dissipatively structure pigments in the visible using visible wavelengths.

Although the composition of Earth's early atmosphere is still highly debated, the scenario presented above is consistent with the bulk of the available geochemical and biochemical data from the era (Kasting, 1993; Lowe and Tice, 2004; French et al., 2015; Meixnerová et al., 2021) and, most importantly, consistent with the very particular and finely tuned UV-C photochemical characteristics preserved in the fundamental molecules of life. These include their very strong UV-C absorption and extremely rapid dissipation of the electronic excited state energy into heat through a conical intersection to internal conversion (see Fig. 3 of our article under discussion and Michaelian, 2021).

The fully developed methanogens that Björn refers to, capable of filling the atmosphere with methane, would not, of course, have been around at the origin of life but perhaps 500-700 million years later (Lowe and Tice, 2004). At this point, complex biosynthetic pathways would have evolved, allowing dissipative structuring of pigments in the visible using, for example, the free energy accumulated from various visible photons and stored in ATP molecules. The intensity of the solar spectrum at Earth's surface as a function of time since present, including the effects of solar evolution, plate tectonics, and methanogen CH₄ production, leading to a period of atmospheric haze between 3.2 and 2.7 Ga, was, in fact, discussed in our original article and presented in Figs. 2 and 3 (Michaelian and Simeonov, 2015).

Björn seems to favor a hydrothermal-vent, bottom-ofocean, theory for the origin of life. However, Stanley Miller convincingly argued (Miller and Lazcano, 1995) that hydrothermal vents are regions of molecular destruction and not molecular creation. In fact, other than simple amino acids and fatty acids, no fundamental molecules have ever been produced in experiments simulating hydrothermal vents. On the other hand, numerous experiments demonstrate routes to most of the fundamental molecules using UV-C light

K. Michaelian and A. Simeonov: Reply to Björn

and common precursor molecules such as HCN and CO_2 (see Michaelian, 2021, and references therein). Furthermore, bottom-of-ocean hydrothermal-vent scenarios lead to the very difficult problem of explaining the very rapid appearance of photosynthesis (perhaps arising only a few million years after the origin of life; Mulkidjanian et al., 2006; Cardona, 2022) and the even more difficult problem of explaining the very particular photon dissipative characteristics preserved in the fundamental molecules (Michaelian, 2021).

3 Present vegetation compared to bare ground

Contrary to Björn's assertion and examples, even beyond the red edge, the albedo of areas covered with vegetation is generally lower than that devoid of life (Barry and Chorley, 2009; Wang et al., 1998; Varotsos et al., 2014; Coakley, 2003). However, as already emphasized, albedo (reflection) alone is insufficient to determine entropy production. Wavelength-dependent reflection, transmission, absorption, and emission must be considered in a careful calculation, as performed, for example, in Michaelian and Cano (2022). The result is that forests are 1.45 times more effective than a sand and rock desert at entropy production due to photon dissipation. Furthermore, natural "bare ground", even over the recently formed volcano in Björn's example, is usually not devoid of life or of life-produced (biological) pigments. Biocrusts form rapidly and significantly reduce the albedo of the rock and soils they cover (Ustin et al., 2009). An important cyanobacterial pigment reducing albedo significantly is scytonemin (Couradeau et al., 2016).

Infrared temperature measurements, obtained from airplane flyovers, support our assertion that life, ecosystems, and the biosphere increase entropy production (Schneider and Kay, 1994). Temperature measurements over climax ecosystems are lower than those measured over perturbed ecosystems, and these are lower than those measured over regions devoid of life. This can be observed in the fact that rocks (or ground without organic material) become much hotter (emit at shorter wavelengths) under the Sun than vegetation does. By expending free energy to convert liquid water in the leaf into a gas, which then condenses at the cold cloud tops, releasing far-infrared photons, the water cycle increases further still photon dissipation. It is the redshifted emission and the association of life with water and the water cycle that are very important to global entropy production (Michaelian, 2012b). This fact should not be conveniently or judiciously ignored.

Clouds, because of high albedo, do reduce entropy production locally, but they are an unavoidable part of the water cycle which allows water, and thus entropy-producing pigments and ecosystems, to spread over land far from ocean shores.

4 The temporal aspect

Forests, as Björn correctly indicates, are sometimes buried and later burned as fossil fuel by humans. However, during their lifetime, trees produce at least 1000 times more entropy than obtained by being consumed as fossil fuel today since less than 0.1 % of the free energy in sunlight goes into carbon bond making, which is how photosynthesis stores free energy (Gates, 1980). Thus, in living plants, more than 99.9 % of solar photon free energy is simply dissipated into heat in the leaves (involving the process of photosynthesis itself, plus non-photochemical quenching). This heat of dissipation is then coupled by the living system to the water cycle through evapotranspiration from leaves, further increasing the photon dissipation or entropy production of the ecosystem or, more globally, the biosphere (Michaelian, 2012b).

The fact that a very small amount of free energy available in sunlight is not instantly dissipated by ecosystems, and instead is stored for different amounts of time, has no bearing on the point under discussion concerning whether or not pigments, life, and ecosystems arose as a result of the thermodynamic imperative of photon dissipation. Storage of free energy for later use is, of course, necessary for maintaining the different trophic levels of an ecosystem, and this hierarchy can be shown to improve global photon dissipation (Michaelian, 2016).

Although the storage of a very small amount of free energy in a practically inaccessible form (for example, deposited underground as coal or petroleum) may make ecosystems imperfect at dissipation, so too does the fact that (1) their photon absorption is not complete (albedo is not zero); (2) their emissivity is not maximal; (3) the physical sizes of the pigments are not at their theoretical limit; (4) fluorescence reduces entropy production – i.e., the quantum efficiency for de-excitation through a conical intersection for internal conversion to the ground state could be further increased; and (5) pigment distribution over the whole Earth surface could be further improved. In other words, ecosystems still have room to evolve under the thermodynamic imperative towards becoming even better dissipating systems.

Modern ecosystems are, however, much more effective at dissipating sunlight than were ancient ecosystems, which can be seen from (1) the appearance of new pigments over time covering even more of the solar spectrum (Michaelian and Simeonov, 2015); (2) the spread of life over the entire Earth surface and the increase in biomass over time (Benton, 1978); (3) the observation that vegetation increases water vapor in the atmosphere (Kleidon et al., 2000), maintaining day and night temperatures similar, thereby increasing to 4π instead of 2π the solid angle of the Earth's emitted radiation (effectively doubling this part of the entropy production); and (4) the fact that greater biodiversity of modern ecosystems implies more complete energy dissipation (Buzhdygan et al., 2020). The thermodynamic imperative based on the second law is also driving human activity and evolution. Human free energy use (dissipation) has increased exponentially over the last few centuries, and this trend is projected to continue for as long as we remain a viable knowledge-possessing species. Our future contribution to global dissipation will almost certainly go much beyond our present dissipation of the chemical potential stored in fossil fuels or beyond our animal role as gardeners for the photon-dissipating plants (e.g., fertilizers and seed spreaders). We have already significantly increased the entropy production of Earth through global greening (Piao et al., 2020) and look soon to be capable of terraforming other planets.

5 Aquatic environments

The data presented by Björn on light reflection from different water bodies, with and without organic material (their Figs. 4 and 5), are entirely consistent with our assertion that life on water surfaces increases entropy production, principally through short wavelength photon dissipation. As emphasized, both the wavelength-dependent absorptivity and emissivity are needed to calculate the entropy production (see Michaelian and Cano, 2022). Albedo measurements alone are inadequate. Absorption and dissipation into heat of the shorter incident wavelengths contributes more to entropy production. It is not the energy or the number of photons that is relevant to nature's thermodynamic imperative, but rather the dissipation of free energy, and this quantity depends not only on the reflected, but also on the absorbed and emitted spectra.

Living organisms and free-floating, biologically derived organic pigments - colored dissolved organic matter - at the ocean surface microlayer certainly do augment photon dissipation (entropy production) compared to water without organic material by (1) increasing photon absorption at the surface, particularly for shorter wavelengths and shallow incident photon angles, and (2) increasing the redshift of the emitted spectrum by coupling it to evaporation from the ocean surface microlayer (see Michaelian, 2012b, and references therein). A detailed calculation of the entropy production as a function of incident photon wavelength for the ocean surface microlayer, with and without organic material, is given in Sect. 6 of Michaelian (2012b). By absorbing and dissipating UV and visible light, the organic matter at the ocean surface microlayer contributes an additional approximately 23 % to the total entropy production due to photon dissipation in this layer on a clear day and a surprising 400 % on an overcast day (Michaelian, 2012b).

6 Ice and snow

At least for these materials, it appears that Björn is in agreement with us that life does indeed increase photon dissipation.

7 Conclusions

Björn assumes that albedo (reflection) is the only important factor related to entropy production due to light interaction with pigments in living organisms, ecosystems, and the biosphere. He ignores the other components involved in photon dissipation in vegetation mentioned in our original article and abstract: (1) the shift towards the infrared of the emitted spectrum (wavelength dependence of the emissivity), (2) photon emission into a greater solid angle due to similar day and night temperatures as a result of the increase in atmospheric water vapor attributable to vegetation, (3) the coupling of life to other photon-dissipating processes such as the water cycle, and (4) the covering of all of Earth's surface with pigments and water. His conclusions are therefore incorrect and thus do not provide a legitimate reason for doubting our assertion that we have presented evidence that supports the thermodynamic dissipation theory of the origin of life (Michaelian, 2009, 2011, 2016, 2017, 2021).

Our theory asserts (i) that life arose as the dissipative structuring and proliferation of pigments under UV-C light to carry out the thermodynamic imperative of dissipating the entropically most important part of the surface solar spectrum (the shortest wavelength photons) prevailing at Earth's surface and (ii) that this irreversible process evolved and coupled to other irreversible abiotic processes, such as the water cycle, to increase the redshift of the globally emitted spectrum, to dissipate even more completely the entire electromagnetic spectrum, and to cover even more of Earth's surface.

Since our first articles published on the topic beginning in 2005 (Michaelian, 2005, 2011), we have continued to uncover more evidence supporting a connection between photon dissipation and the origin and evolution of life. This includes the fact (1) that many of the fundamental molecules of life strongly absorb UV-C light in exactly the wavelength region that was arriving at Earth's surface during the Archean (Michaelian, 2012a, b; Michaelian and Simeonov, 2015; Michaelian, 2016); (2) that many of the fundamental molecules of life possess conical intersections for rapid radiation-less dissipation of the photon-induced electronic excitation energy (Michaelian, 2017, 2021); (3) that efficient photochemical routes to production of the fundamental molecules from simple and common precursors, such as HCN, cyanogen, and CO₂ in water, under UV-C light have been found and that these routes have the hallmarks of dissipative structuring (Michaelian, 2017; Michaelian and Rodriguez, 2019; Michaelian, 2021; Hernández and

K. Michaelian and A. Simeonov: Reply to Björn

Michaelian, 2022); (4) that we have discovered a DNA and RNA enzyme-less denaturing mechanism involving UV-C photon dissipation (Michaelian and Santillan, 2019); (5) that the homochirality of life can be explained from the morning/afternoon ocean surface temperature asymmetry and UV-C photon circular polarization at the ocean surface and the temperature dependence of UV-C-induced denaturing (Michaelian, 2018); (6) that the strong chemical affinity of the UV-C absorbing amino acids (the aromatics), and others, to their codons and anticodons can be explained based on the thermodynamic selection of greater photon dissipation afforded to the complex (Mejía Morales and Michaelian, 2020); (7) that dissipative structuring of the fundamental molecules under UV-C light provides a simple explanation for their existence in space as well as on other astronomical bodies (Michaelian and Simeonov, 2017); and (8) that plants appear to optimize evapotranspiration (the water cycle) over photosynthesis (see Michaelian, 2012a, b, and references therein).

We thank Lars Björn for his comment and welcome and appreciate all challenges to our thermodynamic dissipation theory for the origin and evolution of life.

Data availability. Data within author articles cited in this reply will be made available on reasonable request via email: karo@fisica.unam.mx.

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K. Michaelian and A. Simeonov: Reply to Björn

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