

# Ozone and life on the Archaean Earth

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The trace gas ozone, produced in the present-day stratosphere, acts as a screen for UV radiation between 195 and approximately 290 nm, depending on its column abundance. On the anoxic Archaean Earth, such an ozone screen would not have existed. Although the presence of other screens, such as an organic haze, might have ameliorated the UV radiation flux, even assuming the worst-case scenario (no UV screen), it can be shown that early land masses and the photic zone of the oceans could have been colonized, suggesting that: (i) high UV radiation would not have prevented the colonization of land and (ii) it is unlikely that the fossil record can be used to constrain estimates of the UV radiation environment of the early Earth (although geochemical approaches and the study of extrasolar planetary atmospheres are likely to provide empirical constraints on the early photobiological environment).

**Keywords:** ultraviolet radiation; ozone; Archaean; photosynthesis

## 1. Introduction

On the present-day Earth, ultraviolet radiation is an important stressor for surface-dwelling life (Tevini 1993; Cockell & Blaustein 2000), and particularly for the very organisms that must be exposed to the Sun's solar radiation for their energy requirements—phototrophs (Falkowski & Raven 2007).

Ultraviolet radiation imparts energy to complex macromolecules, which causes lesions detrimental to their function. For molecules such as proteins and lipids, provided the rate of cellular de novo synthesis exceeds the rate of UV-induced damage, this damage is mainly manifested as an energetic cost to the cell (except for other indirect effects, such as free radicals from damaged proteins causing damage to DNA; Campbell *et al.* 1998). However, damage to DNA is heritable, and if the lesions, for example cyclobutane pyrimidine dimers, are large in number or in critical locations in the genome, it can be lethal to the cell (Jagger 1985; Gascon *et al.* 1995). Thus, it is understandable that a strong selection pressure has existed for the innovation of effective repair and protection processes in surface-dwelling life. A diversity of UV-screening compounds have now been characterized, such as scytonemin, a UV-screening compound found in

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One contribution of 18 to a Discussion Meeting Issue 'Trace gas biogeochemistry and global change'.

terrestrial cyanobacteria (Dillon & Castenholz 2002; Dillon *et al.* 2002), and mycosporine-like amino acids (Karentz *et al.* 1991; Garcia-Pichel & Castenholz 1993), found in a diversity of organisms. The photolyase, light-dependent DNA repair system is a phylogenetically widely distributed, and apparently ancient, nucleic acid repair pathway (Grogan 1997; Essen & Klar 2006).

Ultraviolet radiation below 195 nm does not reach the surface of the present-day Earth on account of the presence of oxygen and carbon dioxide (Ogawa 1971; Yung & DeMore 1999). On the anoxic Archaean Earth (Catling & Claire 2005), carbon dioxide would have screened wavelengths below approximately 195 nm. On the present-day Earth, wavelengths below approximately 290 nm (under an ozone column abundance of approx. 300 Dobson units) are screened by ozone, synthesized in the stratosphere by the photochemical conversion of oxygen (Cicerone 1987).

In the absence of any other UV radiation screens, it has, for a long time, been recognized that the penetration of short-wavelength UV radiation (primarily UVC radiation between 200 and 280 nm) to the surface of an anoxic Archaean Earth could have had important consequences for exposed surface-dwelling life (e.g., Sagan 1973; Margulis *et al.* 1976; Rambler & Margulis 1980). The ‘Berkner–Marshall’ hypothesis first posited that the formation of an ozone shield was necessary for the colonization of the land masses (Berkner & Marshall 1965).

Recently, geochemical evidence for microbial mats on land at *ca* 2.6 Gyr ago has been suggested as evidence for the existence of an ozone shield at that time, much earlier than the inferred date of the ‘Great Oxygenation Event’ *ca* 2.4 Gyr ago when atmospheric oxygen levels rose (Watanabe *et al.* 2000), the assumption being that the lack of UV radiation screening would have otherwise prevented the colonization of land. More recently, fossil evidence for an Archaean surface-dwelling microbial mat has been used to attempt to infer the ultraviolet environment of the early Earth (Westall *et al.* 2006).

This previous work raises two general questions: (i) could UV radiation have prevented the colonization of land by phototrophs, even assuming that they lacked biological UV-screening compounds (a worst-case assumption) and (ii) can the morphological fossil record provide constraints on the UV radiation environment of the early Earth?

## 2. UV flux on early Earth—the worst case

As a useful approach to understanding the photobiological environment of the Archaean Earth, it is reasonable to investigate the biological consequences of the worst-case scenario—a retreat from this position will allow for a more clement photobiological picture of the early Earth. Furthermore, this allows us to evaluate the notion that life on Archaean land must imply a clement UV radiation regimen. The worst-case scenario is an anoxic Earth (lacking an ozone shield) with no other UV absorbers in the atmosphere, other than, of course, carbon dioxide screening wavelengths below 195 nm (the assumption of carbon dioxide in the early atmosphere seems safe). Other bulk gases such as nitrogen will contribute to UV radiation scattering, but they do not provide any specific cut-off in wavelengths reaching the surface of the Earth.

Previous suggestions for other UV radiation absorbers in the early atmosphere have included a hydrocarbon smog (Sagan & Chyba 1997; Kasting *et al.* 2001; Pavlov *et al.* 2001), which could have been produced from the methane evolved by methanogens, and a sulphur haze (Kasting *et al.* 1989). For the purposes of investigating a worst-case scenario, we will assume that they did not exist.

### 3. Consequences for early life

The question of whether the lack of an ozone shield in the Archaean atmosphere would have prevented the colonization of the land masses can be rephrased as: if we assume the worst-case flux, are there zones within physical substrates that could have been clement to phototrophs with respect to radiation exposure? We considered phototrophs because they are a ‘worst-case organism’—they must be exposed to solar radiation to gather sufficient photosynthetically active radiation (PAR) for growth (Cockell & Raven 2004). We use physical substrates to examine the implications of the UV flux because this makes the minimum assumptions about the biological screening capabilities of these early organisms (i.e. we are assuming the worst-case that they had none). We will assume that the organisms had UV-repair processes, partly because many of these processes, such as photolyase repair, appear to be very deep branching and partly because if they did not, the organisms would have been unable to tolerate any UV radiation exposure at all since screening, either biological or physical, cannot be completely effective.

To determine the region within a physical substrate suitable for phototrophs, we set the upper level as the point where UV-induced damage to DNA would be the same as that at the equator of the present-day Earth at vernal equinox at midday. By taking a level of UV radiation under which a diversity of organisms on present-day Earth are known to survive and grow, we are making a conservative estimate, but obviously survival and growth under UV radiation levels much higher than the Earth’s equator would expand the zone of photosynthetic potential.

The lower level of the zone can be taken to be the level at which the PAR is the minimum required for photosynthesis (Raven & Cockell 2006). Red macroalgae have been found, apparently growing photolithotrophically, at a depth of 274 m in the ocean (Littler *et al.* 1986) where PAR would be approximately  $10 \text{ nmol m}^{-2} \text{ s}^{-1}$ . Raven *et al.* (2000) calculated the minimum light level required for growth using  $\text{O}_2$ -evolving photosynthesis based on the effects of the back-reactions and found this to be in excess of the approximately  $10 \text{ nmol m}^{-2} \text{ s}^{-1}$  suggested from the observations of Littler *et al.* (1986).

Raven *et al.* (2000) considered three back reactions in growth dependant on photosynthesis. They are: charge recombination in photosystem two, which competes increasingly with forward electron transport as incident PAR decreases; proton leakage through the photosynthetic membrane which increasingly competes with the ATP-producing flux of protons through the  $\text{CF}_0\text{CF}_1$  ATP synthetase at low PAR; and the breakdown and re-synthesis of proteins.

As these reactions occur in series, with protein resynthesis depending on the leak-prone ATP-generating reaction, which in turn depends on the product of the back-reaction prone photosystem two, the theoretical overall minimum level of PAR for growth supported by  $\text{O}_2$ -evolving photosynthesis is in excess

of  $0.1 \mu\text{mol m}^{-2} \text{s}^{-1}$  (Raven *et al.* 2000). Data that were overlooked (Paula *et al.* 1996) or that have since been published (Hausse *et al.* 2002; Inoue 2003; Quigg & Beardall 2003; Quigg *et al.* 2003, 2006) do not alter this conclusion. The minimum PAR required for photolithotrophic growth of  $\text{O}_2$ -evolving organisms will be considered here to be approximately  $0.1 \mu\text{mol m}^{-2} \text{s}^{-1}$ , substantially lower than light levels often found at the 1% light level depth (equivalent to approx.  $20 \mu\text{mol m}^{-2} \text{s}^{-1}$  at midday in many locations on Earth).

(a) *Land habitats for early life*

We examined the penetration of UV radiation and PAR into three microhabitats that are known to contain phototrophs on present-day Earth. They are as follows.

- (i) *Soils containing ferric iron impurities.* Iron has been proposed as a screen to the Archaean Earth (3.8–2.5 Gyr ago; Olson & Pierson 1986; Pierson *et al.* 1993; Bishop *et al.* 2006).
- (ii) *Halite (NaCl) crystals.* During evaporation and precipitation of salts within topographic depressions, halite and other salts such as gypsum would be an expected product. On Earth, halite/gypsum encrustations in intertidal regions and at the edges of lakes are known to be the habitats for ‘endoevaporitic’ organisms (Rothschild *et al.* 1994; Oren *et al.* 1995). Buick & Dunlop (1990) document an Archaean gypsum evaporitic environment, providing direct evidence at least for the presence of potentially habitable evaporitic environments.
- (iii) *Rocks.* A diversity of rock types, including sedimentary rocks, such as sandstones (Nienow *et al.* 1988), and crystalline rocks fractured by asteroid and comet impacts (Cockell *et al.* 2002), provide microenvironments for cryptoendolithic micro-organisms, provided they possess sufficient permeability for the formation of biofilms.

To investigate iron-shielding, transmission of light from 200 to 700 nm was measured through a 0.5 mM solution (1 cm light path) of  $\text{FeCl}_3$  and it was used to derive an attenuation function for ferric iron in solution. To modify this attenuation spectrum for use in the radiative transfer model, we assumed that the sediments covering the organisms have a density of  $3 \text{ g cm}^{-3}$ . These values are typical of many iron-containing sediments (Korbel & Novak 2002). We assumed that a typical ferric iron mineral might contain 0.1% by weight of iron. This might be on the low side, for example a mineral such as riebeckite contains just over 10% ferric iron, but it will serve to illustrate that even low concentrations of ferric iron can provide an effective UV screen (and we assume that the mineral may be mixed with many other non-iron-containing minerals such as quartz or gypsum).

Our theoretical model uses laboratory solutions of ferric iron, not the raw minerals. Since the iron solution does not absorb PAR, the model predicts that the PAR remains constant through the material, which is not realistic as many minerals will attenuate PAR, if only by scattering. We have assumed that PAR drops by an order of magnitude every 2 mm depth into the sediment, based on light penetration through quartz sand (Lassen & Jørgensen 1994).

To examine transmission through halite, its crystals were precipitated onto a UV-transmitting quartz cover-slip to a thickness of 1 mm by evaporating a 1 M solution of NaCl at 60°C. The crystals precipitated as a white mass of sub-millimetre-sized crystals. The transmission was measured from 200 to 700 nm and the experiment was repeated three times to derive a mean attenuation function for this material.

To investigate attenuation through rock, we measured the mean attenuation of light from 200 to 750 nm through four pieces of gneissic rock shocked by an asteroid impact (described in [Cockell & Raven 2004](#)). They were cut to 1 mm thickness. We consider it here to be a generalized approximation of a shocked, heavily fractured habitat on the early Earth. The exact attenuation properties of different rock types, even individual specimens, will, of course, vary ([Nienow \*et al.\* 1988](#)) and iron-containing rocks will more effectively screen UV radiation (see above). The low-iron, but fractured, gneiss is a model for a worst case (UV reduction mainly caused by scattering with low absorption).

In our attenuation calculations, we did not distinguish between absorption and scattering in the substrates, but instead used the attenuation properties obtained in the laboratory, and we assumed an exponential decline of light transmission through the material.

Attenuation was measured using radiation provided by a 150 W xenon-arc lamp source (Cairn Research, Kent, UK). The measurements of attenuation were made using an S-2000 spectrometer (Ocean Optics, FL, USA) fixed under layers of the materials being investigated. The attenuation properties of the iron compounds, halite and fractured gneiss were incorporated into the radiative transfer model and the attenuation properties were the mean of at least three independent measurements. The standard deviation was less than 10% in each of the cases.

### *(b) Radiative transfer calculations*

To calculate the UV flux on the surface of the Archaean Earth, we used a simple UV radiative transfer model described previously ([Cockell 2000](#)). The solar flux at the surface of the Earth was calculated by a  $\delta$ -2 stream method, whereby the direct term is represented by Beer's law and the diffuse term is calculated according to a Delta-Eddington approximation. This radiative transfer approach has been described in detail previously (e.g. [Joseph \*et al.\* 1976](#); [Haberle \*et al.\* 1993](#)).

The extraterrestrial spectrum measured in Earth orbit and provided by [Nicolet \(1989\)](#) was used to calculate the extraterrestrial spectrum incident on the top of the atmosphere. The radiative transfer model has a resolution of 2 nm. A 25% less luminous Sun was assumed for the time *ca* 3.5 to 3 Gyr ago ([Newman & Rood 1977](#); [Gough 1981](#)). This assumption turns out to be not too important because the overwhelming difference in the UV-induced DNA damage between Archaean and present-day Earth is caused by the presence of short wavelengths of UV radiation and their disproportionate ability to induce DNA damage when compared with longer wavelengths, not the absolute UV flux.

As we wish to investigate light levels for photosynthesis under worst-case UV fluxes, we have assumed cloudless and dust-free skies. The concentration of nitrogen was assumed to be the same as the present value of 0.8 bar.

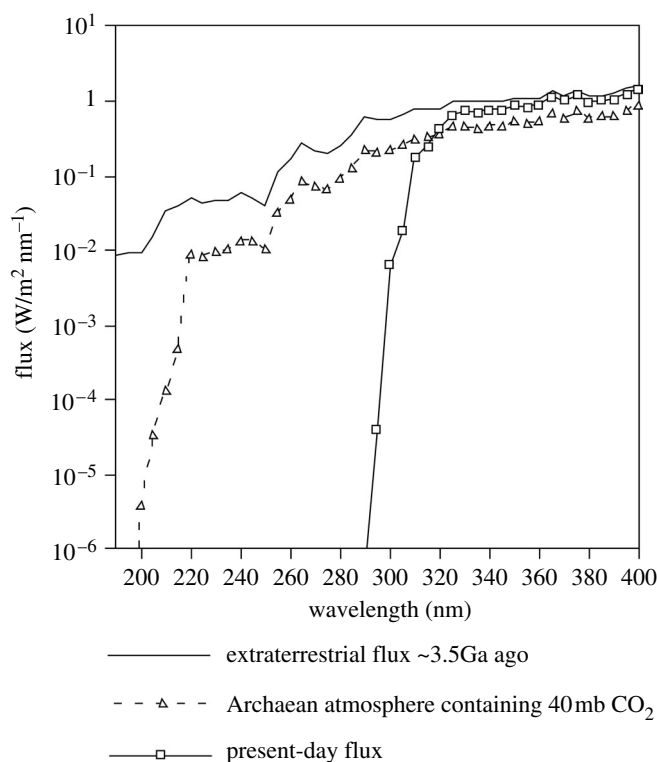


Figure 1. Calculation of the UV flux on the Archaean Earth (a worst-case assumption with no UV-absorbers and 40 mbar CO<sub>2</sub> in the atmosphere). Also shown is the model flux on the present-day Earth (sun at a zenith angle of 0°).

An atmospheric partial pressure of CO<sub>2</sub> of 40 mbar was chosen for the Archaean. This is based on iron precipitation patterns in Precambrian paleosols 2.8–2.2 Gyr ago (Rye *et al.* 1995). Calculations using the silicate–carbonate equilibrium also predict that pCO<sub>2</sub> was less than 150 mbar (Mel'nik 1982) at this time. These values may have been higher 3.5 Ga ago. However, assuming the lower value takes a worst-case scenario for UV flux (i.e. the minimum contribution to scattering by CO<sub>2</sub>). The UV flux experienced under this worst-case scenario is shown in figure 1.

The effect of UV radiation on a biological system is represented by an action spectrum ( $\epsilon[\lambda]$ ). This is a plot of relative biological effect (usually some measure of damage) against the wavelength of radiation. Action spectra below 280 nm are not generally measured since wavelengths less than 280 nm are not ecologically relevant on present-day Earth. We convolved the DNA absorbance profile from 195 to 280 nm (Horneck 1993) with the standard DNA action spectrum at wavelengths greater than 280 nm (Green & Miller 1975; see also Lindberg & Horneck 1991) to obtain a generalized DNA action spectrum (figure 2). As DNA is the primary target of UV radiation damage, we take it to approximate the loss of microbial viability, which is validated from studies of action spectra of whole organism loss of viability (e.g. Lindberg & Horneck 1991).

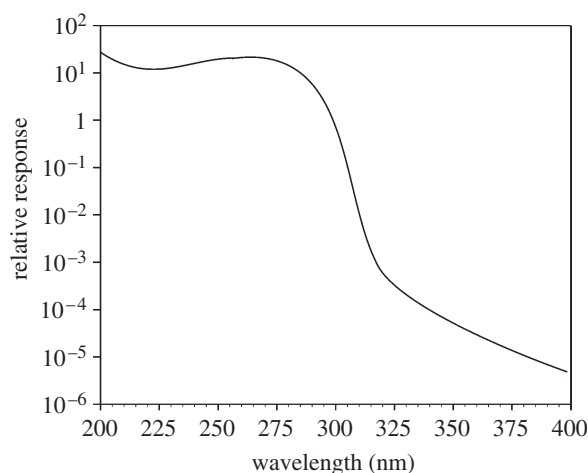


Figure 2. DNA action spectrum used to calculate UV-induced damage to DNA.

The product of the action spectrum (here arbitrarily normalized to 300 nm) and the spectrum of the incident radiation ( $E[\lambda]$ ) provides the biologically weighted spectral irradiance ( $\varepsilon[\lambda]E[\lambda]$ ). Numerical approximation of the integral of these curves provides the biologically effective irradiance at a given instant in time.

The depths at which UV-induced damage is similar to the surface of the present-day Earth and at which PAR is at the theoretical minimum required for photosynthesis were calculated.

### (c) Zones of photosynthetic potential

Biologists often use the depth at which light levels are reduced to 1% of incident PAR as a measure of the potential lower depth of photosynthesis in various media and substrata (the ‘compensation point’; Falkowski & Raven 2007). However, photosynthesis can occur at much lower depths than this. Even taking a lower PAR limit as  $0.1 \mu\text{mol m}^{-2} \text{s}^{-1}$ , the radiative transfer model suggests the existence of zones suitable for phototrophs under an ozone-free atmosphere (figure 3). If the lower limit for photosynthesis is  $10 \text{ nmol m}^{-2} \text{s}^{-1}$ , then the lower limit of these zones drops and the region suitable for phototrophs within any given microhabitat is expanded.

Life in shocked gneissic rock would have to be below the compensation point to achieve DNA-damage levels similar to those on Earth. However, under ferric iron sediments, the iron is such an efficient absorber of UV radiation that it is possible to be within the euphotic zone (the zone above the compensation point where light levels are greater than 1% of incident) and have UV damage levels lower than those on present-day Earth. These results are consistent with those of Olson & Pierson (1986) who showed that a 1 mm layer of iron sediment would be sufficient to create a screen with a transmission of only 3% at 265 nm.

We also found halite encrustations to be an effective screen, but because the crystals scatter radiation and not because NaCl is an effective UV absorber. Similarly, gypsum and calcite are not effective UV absorbers in the region of the UV spectrum. Protection under these salts would depend upon scattering and/or



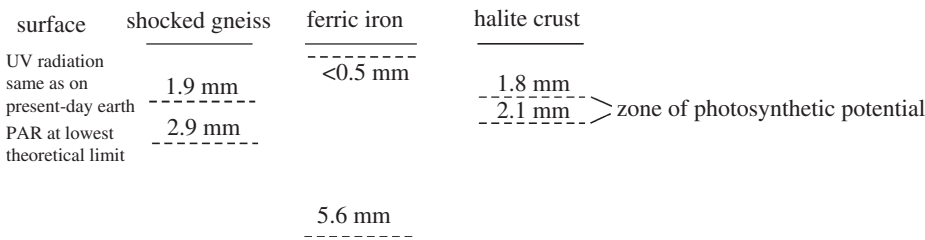


Figure 3. Zones of photosynthetic potential on Archaean land under a worst-case assumption of UV radiation conditions.

the presence of UV-absorbing contaminants such as iron. When precipitated as a mass of small crystals, halite could provide a radiation environment on the early Earth that is suitable for phototrophs.

The zone of photosynthetic potential will be influenced by the attenuation properties of the material considered. As rocks containing iron are more effective at absorbing UV radiation than those without, the zone in these rocks will be at a shallower depth.

The calculations presented here are supported by simple considerations of the order of magnitude of expected radiation fluxes. The PAR levels on the early Earth, at midday at vernal equinox at the equator, would have been about 10 000 times greater than the minimum required for photosynthesis, even assuming a 25% less luminous Sun. The UV damage, measured as a DNA-weighted irradiance, in a worst-case scenario (clear skies and no UV-screens) would have been about 1000 times greater than the levels found on the surface of the present-day Earth. Therefore, it follows that under any substrate where there was not a preferential attenuation of PAR compared to UV radiation, there would likely have been a favourable environment for phototrophs (although varying PAR/UV ratios at different latitudes, times of day and seasons would obviously change the characteristics of these zones; for example, the depth of the zone will change over seasonal time-scales as PAR and UV intensities change). We have considered the highest PAR and UV levels, and thus the maximum depth of the zone.

The upper level of the photosynthetic zone also defines the point below which UV damage is less than that on present-day Earth for non-photosynthetic organisms. Since they do not require visible light for energy, any depth below this level can be considered favourable for them.

A recent work on the effects of a simulated Martian UV flux, which has a similar spectral distribution to that supposed here for the Archaean Earth, has shown that the damaging effects of UV radiation occur at depths where the UV flux has been extinguished (Hansen *et al.* 2005). The authors attribute their observations to indirect effects of UV radiation, such as free-radical production. Thus, the zones described here might still have been relatively inclement when compared with greater depths, with the possible requirement for defences against free-radical production in early phototrophs that took advantage of these zones.

In summary, the calculations suggest that on land masses, even under the worst-case assumptions of UV radiation (no ozone screen, no other atmospheric UV-screen other than CO<sub>2</sub>, and minimum CO<sub>2</sub> concentration), photosynthesis



could have been sustained in zones of microhabitats, even if organisms had UV repair capabilities no better than today and we assume that there was no biological screening (including the matting habit).

This finding is significant because it suggests that the presence of life on land 2.4 Gyr ago cannot be correlated with the absence or presence of atmospheric UV radiation screens (cf. Watanabe *et al.* 2000). Such screens would only have influenced the efficacy of protection and repair processes that would have been required.

#### 4. The fossil record and the photobiological environment of the early Earth

The point presented by Watanabe *et al.* (2000) raises a further important fundamental scientific question—can the fossil record ever be used to constrain the UV radiation environment on the surface of the early Earth? The answer to this question affects the extent to which we can correlate the morphology and nature of Archaean microfossils with their radiation environment (Westall *et al.* 2006).

Consider a scenario where an isolated, planktonic organism was found in the Archaean fossil record. Further, it could be shown, by virtue of the preservation context, that this organism did not use any physical UV radiation protection, it was photosynthetic and needed to live in a near-surface environment. Consider also that the organic preservation of the fossil was so remarkable that it could be demonstrated that it never produced UV-screening compounds (this level of organic preservation is implausible, but this is a thought experiment). Would this exposed ‘end-member’ organism provide any constraint on the UV radiation environment?

Some non-marine organisms such as *Deinococcus radiodurans* can tolerate high instantaneous UV fluxes (e.g. Lavin *et al.* 1976; Caimi & Eesenstark 1986). Gascon *et al.* (1995) examined the UV radiation tolerance of *D. radiodurans* under a  $1.7 \text{ W m}^{-2}$  UV radiation source, emitting primarily at 254 nm. They demonstrated dose tolerances of up to  $400 \text{ J m}^{-2}$  without significant loss of viability. The dose estimates they derive are similar to those measured under a 254 nm UV source by Caimi & Eesenstark (1986). If the UV source of Gascon *et al.* (1995) is weighted to the DNA action spectrum value at 255 nm, then the organisms in these experiments are being subjected to an equivalent DNA-effective irradiance of approximately  $45 \text{ W m}^{-2}$ , about half to a third that of the worst-case instantaneous dose on the surface of Archaean Earth (Cockell 2000).

For the purposes of this calculation, let us assume that the mean depth at which our end-member organism lives in the Archaean oceans is approximately 50 m, the depth at which UV radiation could be reduced to approximately 0.1%, based on measurements in clear Antarctic water (Smith & Baker 1981; Smith *et al.* 1992), but where PAR would still be sufficient for photosynthesis. Organic matter acts as a strong UV absorber (Bricaud *et al.* 1981; Kirk 1994), but we will assume clear waters (a worst-case scenario). The average weighted instantaneous UV exposure might therefore be approximately  $0.1 \text{ W m}^{-2}$ . *Deinococcus radiodurans* could tolerate the exposures in the experiments described previously for at least 5 min. Ignoring the non-marine phylogeny of *D. radiodurans* and using it is an analogue for cellular repair processes in our organism; then, it could survive in such a habitat for 40 h—longer than the length of the Archaean day.

This calculation assumes repair processes no better than organisms found on present-day Earth, but clearly, for organisms on the early Earth subjected to a higher UV flux, there would have been the potential for a selection pressure for more effective repair processes.

This simple calculation illustrates the principle that the lack of an ability to directly assess the DNA repair capabilities of Archaeal micro-organisms prevents the fossil record from being used to draw inferences about the UV radiation environment of the early Earth. An isolated, planktonic phototroph found in the fossil record would not suggest a clement UV radiation environment.

The other end-member fossil—one associated with the matting habit or an endolithic habitat, where biological or physical screening appears to have been available—similarly provides no suggestion of a high UV flux because these growth habits are found even on the present-day Earth, although clearly they could have provided protection under a high Archaeal UV flux as described earlier.

Thus, both isolated planktonic and physically and biologically shielded phototrophs could have existed on an Archaeal Earth with a UV flux similar to the present-day Earth or on one with the highest possible UV flux.

Recently, studies of sulphur mass-independent isotope fractionation patterns in the rock record have suggested penetration of short-wavelength UV radiation deep into the Archaeal atmosphere (Farquhar *et al.* 2000). Direct photochemical effects of UV radiation penetrating to the surface of the Earth and preserved in the geochemical record could potentially provide an empirical determination of the UV radiation environment. The direct spectroscopic investigation of the atmospheres of ‘early Earth-like’ planets orbiting distant stars might provide an opportunity to directly investigate plausible atmospheric compositions for the early Earth, and thus its photobiological environment. Thus, other means may provide a way to directly measure the early photobiological environment.

## 5. Conclusion

Under a worst-case UV flux on the Archaeal Earth, the land masses could have been colonized. Assuming repair processes similar to organisms on the present-day Earth, i.e. organisms capable of tolerating the UV flux found on the exposed surface of the present-day Earth, there would have been zones in a diversity of substrates in which phototrophs would be exposed to a UV flux similar to the surface of the present-day Earth, but where PAR would still be sufficient for photosynthesis. Simple calculations show that in certain environments even exposed planktonic phototrophs with effective UV radiation repair could have lived. Thus, the fossil record cannot provide a constraint on the Archaeal UV flux, but the geochemical record or the examination of extrasolar planets might eventually allow these worst-case calculations to be replaced by more direct measurements.

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