MAXIMUM AND EFFECTIVE POTENTIAL DIFFERENCES UNDER A VARIETY OF CONDITIONS

Long-wavelength absorption maximum of pigment (nm)	Ambient temperature (°C)	Distance of source to organism (cm)	μ_o (eV)	μ_{eff} (eV)
1,020	4	0	0.65	0.57
850	4	0	0.79	0.70
1,020	4	15	0.60	0.52
850	4	15	0.73	0.65
1,020	4	50	0.47	0.40
850	4	50	0.61	0.53
1,020	100	15	0.38	0.30
850	100	15	0.48	0.40
1,020	50	50	0.35	0.28
850	50	50	0.48	0.40

berg and Tonge[4] have developed a more general model, but it is more difficult to understand, and gives the same result as that of Ross and Calvin.

According to Ross and Calvin[3], the partial molar free energy difference between the excited pigment and the pigment in the ground state, that is, the maximum chemical potential difference that can be achieved by a photochemical system, is given by:

$$\mu_o = kT\ln[\phi_{lum}\int I_s(\lambda)\sigma(\lambda)d\lambda / \int I_{BB}(\lambda)\sigma(\lambda)d\lambda]$$

where k is Boltzmann's constant, T is the absolute ambient temperature, λ is wavelength, $I_s(\lambda)$ is photon fluence rate (scalar photon irradiance) from the source (in this case the hot vent), $I_{BB}(\lambda)$ is photon fluence rate from thermal black-body radiation at ambient temperature, $\sigma(\lambda)$ is the absorption cross-section of the pigment of the photochemical system that absorbs the radiation, and ϕ_{lum} is the quantum yield of luminescence for the pigment involved, and is assumed here to be 0.3 (the value for chlorophyll *a*). The integrals should be extended over the whole absorption spectrum of the pigment.

For bacteriochlorophyll *b* the wavelength of the absorption maximum is 1.02 μm, and the half-bandwidth about 2 × 25 nm. I approximate the band by a corresponding gaussian function. Following Nisbet *et al.* I shall first assume T_s=650 K (377 °C), and an ambient temperature of 277 K (4 °C). With the hot radiation source extending over 2π steradians, we then obtain a maximum potential difference (μ_o) of 0.64 eV. This does not deviate much from the value (0.65 eV) obtained if one assumes that the pigment absorbs only at the absorption maximum, so the band shape is not critical in this case.

If the system is to drive a flow of electrons, the potential difference must be lower. Following equation (10) of Ross and Calvin[3], we obtain a working potential difference for maximum power storage, μ_{eff}, of 0.56 eV. Note that this value has been obtained under very generous assumptions, namely that the source extends over 2π steradians and intervening water does not absorb any radiation, while ambient temperature is still as low as 4 °C, a rather unrealistic scenario. For a pigment peaking at 850 nm the corresponding μ_o is 0.79 eV and the working potential difference for maximum power storage 0.70 eV.

If we take into account the absorption by water between the source and the organism, the potentials are further decreased. For these calculations I used the absorption coefficients for water of Curcio and Petty[5]. It is, however, quite unrealistic to assume an ambient temperature of 4 °C close to a 377 °C source extending over 2π steradians. I have also considered the more realistic cases of 100 °C at a distance of 15 cm and 50 °C at a distance of 50 cm (see table). An 850-nm pigment seems to give an advantage over a 1,020-nm pigment; however, the possible power storage is the product of absorbed photon flux and potential difference. Because of the higher spectral irradiance of the source at the longer wavelength, the possible power storage with a 1,020-nm pigment is more than 20 times that obtainable with an 850-nm pigment.

In looking for a plausible start for the evolution of photosynthesis exploiting radiation from hydrothermal vents, I believe we should restrict the search to looking for electron transfer reactions that can be driven by a photochemical system limited to a potential difference of about 0.4 eV. As a comparison, the span between the mid-point potentials for the primary electron donors and acceptors of present-day photosynthetic purple bacteria is about twice this value.

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SIR — Nisbet *et al.* in Scientific Correspondence[1] propose that photosynthesis evolved from near-infrared phototaxis that enables chemotrophic bacteria to find hydrothermal vents, as "such places can provide optimal energy that supports life. Organisms that lose touch with such vents risk starvation...".

But that is the situation now, when there is free energy to be gained from combining H_2S from the vent with dissolved O_2. Before water-oxidizing photosynthesis first appeared around 2 billion (2×10^9) years ago, there was no free O_2, and nothing to be gained from occupying dangerously hot places on the ocean floor, as what came out was at redox equilibrium with the ocean. So dismissing "photosynthesis first" on these grounds is a classic example of trying to lift oneself up by the bootstraps.

Even if early chemotrophs gathered at thermal vents to keep warm, there is another problem: anaerobic photosynthetic bacteria have near-infrared-absorbing bacteriochlorophyll today because this window in the spectrum is made available to them by the rather more successful oxygen-evolvers that need higher-energy (visible) light to split water. Before oxygen evolution, it is likely that the greater energy available from visible light was also used by any photosynthetic organism. So we have another problem, a hidden assumption about what is "primitive".

I prefer to think of anaerobic photosynthetic bacteria as deposed monarchs, waiting, in specialized environments below the thermoclines of lakes, until aerobic republicanism has gone out of fashion. But they are alive today: evolution did not come to a halt in purple bacteria, and they are really rather well adapted to their environment. The emission of near-infrared by hydrothermal vents is more likely to have led to thermotaxis evolving from photosynthesis, I should have thought.

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NISBET *ET AL.* REPLY — Both Allen and Björn raise interesting problems. Allen questions the availability of oxidation power in the early Archaean Earth. This is at present a matter of strong debate. The early atmosphere probably suffered major losses of hydrogen to space (significantly from H_2O, leaving oxygen), but it is likely that despite this oxygen source, O_2 partial pressure in the troposphere was low. It is probable, however, that an atmosphere–ocean system dominated by CO_2 and H_2O would have provided oxidation contrast at hydrothermal systems, where the atmosphere–ocean interacts with solutions that have reacted with mantle-derived lava. Thus, hydrothermal systems would indeed have provided habitats for early living communities. This seems to be borne out by the molecular record, which implies that the earliest organisms were exclusively hyperthermophiles[6]. In such a setting, bacteriochlorophyll (which appears to be more primitive than chlorophyll) may have evolved for phototaxis.

We thank Björn for his calculation, which is much more detailed than ours. We stress, however, that we are not proposing that early bacteria lived by infrared photosynthesis from vents. Our suggestion is simply that they developed infrared phototaxis to allow them to detect heat sources at deep-water (for example, mid-ocean ridge) hydrothermal

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