Photosynthesis: Likelihood of Occurrence and Possibility of Detection on Earth-like Planets

R. D. Wolstencroft

Royal Observatory Edinburgh, Blackford Hill, Edinburgh EH9 3HJ, United Kingdom
E-mail: rdw@roe.ac.uk

and

J. A. Raven

Division of Environmental and Applied Biology, School of Life Sciences, University of Dundee, Biological Sciences Institute,
Dundee DD1 4HN, United Kingdom

Although there are considerable technical challenges to be overcome during this decade, the prospects for the detection of Earth-like planets (ELPs) orbiting nearby stars are encouraging. If life has developed on some of the ELPs that may be discovered by sophisticated telescope systems, such as the Terrestrial Planet Finder, the detection of photosynthesis is an attractive possibility. Here we discuss the likely preconditions and subsequent events that have led to the occurrence of O_2-producing photosynthesis on Earth and then extend this discussion to how this may have occurred on ELPs orbiting in the habitable zone of a variety of main-sequence stars from spectral type F0V to M0V. We point out how the need for liquid water and the need to avoid UV radiation have influenced the evolution of photosynthesis on Earth, how the absorption spectra of the dominant (chlorophyll) photosynthetic pigments may have been determined in natural selection, and how and when the evolution of the ability to use water as an electron donor took place. Models for the photosynthetic productivity of ELPs orbiting at the inner edge of the habitable zone are discussed both from aquatic and land-based photosynthesis, making some allowance for global cloud cover on the ELP. The photosynthetic generation of O_2 is greatest on cloud-free planets with hot (e.g., F0V) parent stars, though the advantage over cooler stars depends on the fraction of the planet covered by oceans. The low O_2 generation in ELPs orbiting cooler stars is due to the poor match between the parent star's spectral energy distribution and the assumption of terrestrial pigment properties. We discuss the possibility that a three- or four-photon mechanism might operate on such planets (as opposed to the two-photon system on Earth) and how it could influence the spectral properties of the ELP. We also emphasize the role of tectonic and other geological processes as well as biology in determining the O_2 level on Earth and on ELPs. © 2002 Elsevier Science (USA)

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I. INTRODUCTION

The increasing optimism that Earth-like planets (ELPs) will, in a decade or so, be found to be orbiting a significant fraction of the nearby main-sequence stars has widened the scope for remote sensing of extraterrestrial life from the planets and satellites of the Solar System to include ELPs in planetary systems around such stars (Des Marais and Walker 1999). Plans to detect ELPs orbiting nearby stars using an infrared space interferometer that can null out the light of the central star are being explored by NASA (Terrestrial Planet Finder/TPF) (Beichman *et al.* 1999) and ESA (Infrared Space Interferometer/IRSI). To assist the strategy for the search for ELPs we would ideally like to have some statistical information on the frequency of ELPs that might come from transit experiments such as COROT, KEPLER, or EDDINGTON or from gravitational lensing. Such information could guide the priorities in deciding the dwell times and types of stars that will be surveyed by TPF/IRSI. The other aspect is whether life is likely to flourish, if initially present, given the distance of the ELP and the type of parent star. This is not only a question of whether liquid water could exist at the planetary surface, as encapsulated in the term "Habitable Zone," but also whether organisms on the ELP could find a reliable and long-lived source of energy that would allow them to survive, multiply, and evolve over planetary time scales. Oxygen-generating photosynthesis is such a source of energy which, because it uses water as the electron donor, would be able to provide an abundant source of energy for microorganisms on the ELP.

The detection of photosynthesis on an ELP is an attractive possibility for the remote sensing of extraterrestrial life (Des Marais and Walker 1999). On the assumption (to be analysed below) that photosynthesis on an ELP would lead to O_2 accumulation in its

atmosphere, then the detection of free atmospheric O_2 via spectroscopic detection of O_3 (produced photochemically from O_2) could be used as an indication of the occurrence of life (Leger *et al*. 1993). Such a test is a specific case of the general method for remote sensing of life on other planets suggested by Lovelock (1975), i.e., the detection of gross departures of some chemical component(s) of the planetary atmosphere from thermodynamic equilibrium from other components. While some O_2 can be produced by the (abiological) photochemical dissociation of water, large quantities of O_2 (and hence O_3) require the activity of (biological) photosynthesis. A further possible means of detecting photosynthesis is the spectroscopic remote observation of the pigments which are essential for this process.

Before discussing the possibilities of making the required measurements of O_2 and pigments, we briefly discuss the likely preconditions (Section II) and subsequent sequence of events (Section III) which have resulted in the occurrence of O_2-producing photosynthesis on Earth. This permits us to consider (Section IV) the likelihood that life on an ELP would have led to photosynthesis (potentially detectable by spectroscopy of pigments) and an O_2-evolving variant of photosynthesis (potentially detectable spectroscopically as O_3).

II. ORIGIN AND PREPHOTOSYNTHETIC EVOLUTION OF LIFE ON EARTH

The presence of liquid water is a major prerequisite for life on Earth (or any other planet). Granted the occurrence of adequate water, the requirement that a very significant fraction of this water remains liquid involves a tectonic cycle which recycles the greenhouse gas CO_2. Such a cycle can return CO_2 to the atmosphere even when near-global glaciation restricts the part of the cycle which removes CO_2 from the atmosphere. This can potentially reverse glaciation, the likelihood of which would be increased early in the evolution of life as a result of the lower radiant energy output of the Sun 4 billion years ago than today (Gough 1981, Walker *et al*. 1981). Biogenic methane was probably also a very important greenhouse gas until O_2 increased around 2.3 billion years ago (Kasting *et al*. 2001).

The two current hypotheses as to the origin of life on Earth are the chemoorganotrophic and the chemolithotrophic. The chemoorganotrophic hypothesis has become less popular with the realisation that the early atmosphere was less reducing than was believed in the early experiments on production of organic compounds by atmospheric chemistry (Broda 1975, Chang 1999). The alternative and currently favoured hypothesis is that of a high-temperature chemolithotrophic origin of life (Wächterhauser 1990, Russell and Hall 1997, Pace 1997, Ferris 1999), in which the energy input to the synthesis of organic compounds comes from exergonic inorganic reactions. The evolution of life at hydrothermal vents would also have the advantage of limiting access of UV-B radiation from the young Sun to early life since hundreds of metres depth of seawater would act as a UV-B screen.

The calculations of Jakosky and Shock (1998) suggest that life based on the inorganic chemistry of hydrothermal vents could produce 0.6 M tonnes of organic C per year worldwide. This contrasts with 100 G tonnes of organic C generated today by photosynthotrophs and at least 0.2 G tonnes organic C produced each year by chemolithotrophs on Earth today, mainly using for their exergonic metabolism inorganic substrates which result ultimately from photosynthesis (Raven 1996). The chemolithotrophy on the early Earth which was not associated with continued input of reductant from vents is less readily quantified. However, it would have converted the useable substrates for chemolithotrophy (FeS, H_2S, CO_2; Wächterhauser 1990) into organic carbon and the relatively inert FeS_2 (Russell and Hall 1997), so that there is little possibility of a chemoorganotrophic back reaction oxidising organic C and FeS_2 as oxidant, regenerating the chemolithotrophic substrates.

This depletion of substrates would have restricted the productivity of early chemolithotrophs. This metabolic bottleneck provides both an ecological opportunity for light as an additional energy source and part of the metabolic infrastructure derived from chemolithotrophy, which is used in the various mechanisms of photosynthetic energy conversion found on Earth today.

III. EVOLUTION OF PHOTOSYNTHESIS AND THE ACCUMULATION OF O_2 ON EARTH

For light to be used as the energy source for growth of organisms on Earth requires that they live at the land surface, or at depths of less than 300 m in even the clearest waters, if the light energy supply is to be adequate (Raven *et al*. 2000). This requirement for a certain minimum level of photosynthetically active radiation (PAR) means that the organisms will be exposed to UV-B, exacerbated by the high output of UV-B relative to PAR by the Sun 3.5 billion years ago but, for aquatic organisms, ameliorated by the greater absorption of UV-B than of PAR by natural waters (Cockell 2000, Kirk 1994a,b).

Mulkidjanian and Junge (1997) suggest that the evolution of photosynthesis involved UV-screening proteins in or associated with the plasma membrane. All proteins (and nucleic acids) absorb, and can be damaged by, UV-B; surface-located proteins could screen out some of the UV-B, limiting damage to proteins and DNA within the cell. Excitation energy transfer from the protein to the tetrapyrrol would allow dissipation of this energy as fluorescence, heat, or photochemistry in the earliest evolutionary stages of photosynthesis. The evolutionary selection value of the photochemical alternative for energy dissipation is that the photochemistry could supplement, and ultimately replace, chemolithotrophic reactions as the energy source for growth. This photochemistry would have generated ATP and reductants of relatively low redox potential which could reduce CO_2 to produce organic compounds. Such conversion of reductants such as Fe^{2+} and S^{2-} to Fe^{3+} and S^0 in photosynthetic CO_2 reduction permitted the use of Fe^{3+} and S^0 to act as electron acceptors in respiratory reactions of chemoorganotrophic growth,

regenerating CO_2 and the reductants Fe^{2+} and S^{2-}. However, such recycling would have been limited by the sedimentation of particulate organic C and of particulate oxidants (Fe^{3+}, S^0) which, with tectonic activity, would remove these substrates for anaerobic respiration.

Such depletions of reductants for photosynthesis would have provided a selective advantage for organisms which use the very high potential but abundant oxidant H_2O, with production of O_2. The use of the high-potential reductant H_2O as electron donor for CO_2 reduction involves the use of two photons in photochemistry for each electron transferred from H_2O to CO_2 (Falkowski and Raven 1997). Even with two photons per electron the lower energy per photon at longer wavelengths imposes a limit for photons used in O_2-evolving photosynthesis, which is usually 700 nm but can extend to 730 nm in a few organisms (Halldall 1968, Schiller *et al.* 1997, Koehne *et al.* 1999, Mimura *et al.* 1999). The higher energy per photon at the lower wavelength limit for photosynthesis (380–400 nm) is always converted, after absorption, to the lower energy per photon of longer wavelengths before use in photochemistry.

The evolution of this O_2-producing photosynthesis could have occurred as early as 3.56 billion years ago (Golubic and Seong-Joo 1999, Summons *et al.* 1999, Des Marais 2000), yet the first evidence for *global* oxygenation comes from little earlier than 2.5 billion years ago (Holland 1984, Falkowski and Raven 1997, Brocks *et al.* 1999, Watanabe *et al.* 2000). O_2 accumulation in the atmosphere requires that some of the organic C produced by photosynthesis is removed from the possibility of biological (respiratory) reoxidation by sedimentation. There is evidence that sedimentation of organic C, apparently produced by photosynthesis with H_2O as reductant, occurred well before global oxygenation. Sedimentation of organic C also removes other nutrient elements (such as phosphorus) from the biosphere, so O_2 accumulation coupled to organic C sedimentation also depends on P and other nutrient inputs from weathering processes and thus on continued exposure of unweathered rock by tectonic activity (Algeo and Scheckler 1998, Berner 1998). Tectonic activity is also responsible for returning the carbon sedimented as organic C to the biosphere as CO_2, together with inorganic reductants which consume O_2. On the present Earth sedimentation removes about 0.2 G tonnes of reduced C each year out of 100 G tonnes of primary productivity (Raven and Falkowski 1999).

The long lag between the probable time of evolution of O_2-producing photosynthesis and the global (as opposed to local; McKay and Hartman 1991) accumulation of O_2 in the biosphere involves "missing O_2" which was presumably consumed in the oxidation of residual Fe^{2+} (to Fe^{3+}) and S^{2-} (to S^0 and SO_4^{2-}), including that supplied from hydrothermal vents, possibly at higher rates than today, with Fe^{2+} and S^{2-} from the deep dark ocean mixed with photosynthetic O_2 by ocean circulation (Berner and Petsch 1998, Canfield *et al.* 2000). This suggestion is not easily distinguished from the alternative of oxidation of Fe^{2+} and S^{2-} by anoxygenic photosynthetic bacteria.

Sleep (2001; see also Kump *et al.* 2001) discusses two hypotheses in which the mantle is involved in restricting net burial of Fe_2O_3 in permitting buildup of O_2. The argument is that net removal of Fe_2O_3 from the crust permits the reaction $2FeO + H_2O \rightarrow Fe_2O_3 + H_2$ to proceed, with O_2 removal from the atmosphere by reaction with H_2. Accumulation of Fe_2O_3 at the surface limits H_2 production, allowing O_2 to accumulate. Furthermore, H_2 escape following biogenic H_2 production and photolysis of biogenic CH_4 could have caused irreversible oxidation of early Earth (Catling *et al.* 2001, Hoehler *et al.* 2001).

The final aspect of this consideration of the evolution of photosynthesis on Earth concerns the factors determining the detectability of O_2-producing photosynthesis by remote sensing. Spectroscopy is the only method available, and it could theoretically detect the catalysts of photochemistry (photosynthetic pigments) and one of the products of O_2-generating photosynthesis (O_3, derived photochemically from O_2). Seasonal changes in photosynthetic pigments on the land surface should be detectable from space (with the Sun nulled out) with their characteristic (for Earth) 700-nm cutoff. Photosynthetic pigments in the ocean are less readily perceived in this way.

The next part of this paper (Section IV) considers the likelihood that a similar sequence of events to those described here for Earth could have occurred on an ELP orbiting a nearby star. In terms of observability by spectroscopy from Earth, we need to investigate the likelihood of (seasonally varying) photosynthetic pigments on the land surface in sufficient quantities to be detectable and the likelihood that O_2 would accumulate sufficiently to generate enough O_3 to be detectable spectroscopically as a proxy for O_2.

IV. POSSIBLE ORIGIN AND EVOLUTION OF LIFE AND OF PHOTOSYNTHESIS ON ELPS AND ITS SPECTROSCOPIC DETECTABILITY

We begin by asking how Earth-like an ELP must be and what orbit it must occupy in relation to a particular type of star, if life and photosynthesis of anything like the sort found on Earth are to occur. This latter requirement is defined in terms of the range of distances from a star within which an orbiting planet would be habitable over a period of time; for the Earth this period is (at a minimum) 3.8 billion years ago to the present. This range of distances in relation to a specified time span is known as the Continually Habitable Zone (CHZ).

The assumption made hereafter is that our ELP originally had a $CO_2/H_2O/N_2$ atmosphere (modifiable by living organisms) and that habitability requires the presence of liquid water on the planetary surface. We note that even if oceans form on ELPs, they can also disappear (e.g., Yung and De More 1999), as has occurred on Venus, and that even persistent oceans may not be deep enough to act as effective UV screens (see later in this section). As we saw in Section II the control of temperature on the planet's surface by temperature-independent changes in the atmospheric CO_2 level depends on changes of volcanism and plate tectonic

activity, so these are also requirements for our ELP. Franck *et al.* (2000) have combined volcanism, weathering, and tectonics into a general modelling scheme for identification of the habitable zone (HZ), i.e., the range of distances from a star within which an ELP would be habitable over a long but unspecified time span. However, a significant constraint on such models, pointed out by Whitmire *et al.* (1991), is that low atmospheric temperatures can cause CO_2 condensation, increasing cloudiness via the production of CO_2 ice clouds and thus increasing albedo and decreasing the magnitude of the greenhouse effect of CO_2 via the latent heat release on condensation and its effect on decreasing the adiabatic lapse rate. An effect working in the opposite direction is the greenhouse effect of clouds of CO_2 ice via the scattering of outgoing thermal radiation back up to the surface (Forget and Pierrehumbert 1997). CO_2 condensation thus provides an outer limit for the CHZ, assuming constant stellar luminosity with time (Kasting *et al.* 1993, Kasting 1998).

Tectonic activity can give rise to continental crust and thus to a habitat for land-dwelling biota (Kasting *et al.* 1993, Wetherill 1996). Tectonic activity also permits the preconditions for a chemolithotrophic route at hydrothermal vents. We assume an acidic Fe^{2+}-rich ocean with reducing, H_2S-rich hydrothermal vent water. We also assume that our ELP does not suffer from the climatic extremes which can be associated with chaotically variable, and often extreme, obliquities lacking the stabilizing influence of a large (relative to the planet) satellite (Laskar *et al.* 1993, Williams and Kasting 1997).

The inner limit for the CHZ is determined by the stellar flux at which water loss occurs. Taking the Sun as an example, over the next several billion years the Sun's luminosity will increase, resulting in a modest increase in the water vapour content of the troposphere and a much larger increase in the stratospheric water vapour content (Kasting *et al.* 1993). The increased cloudiness would increase the planetary albedo and a not readily quantified negative feedback could decrease the surface temperature. Neglecting this feedback, when the Sun's luminosity reaches 110% of its current level, catastrophic water losses would occur (in as little as 1 billion years) and habitability would cease ~0.2 billion years later. For low-luminosity M dwarf stars the HZ lies quite close to the star (0.25 to 0.47 AV for an F0V star); because a planet orbiting close to its parent star is forced to rotate synchronously due to tidal forces (Huang 1960), and hence to have one permanently illuminated hemisphere, it has been widely argued that such planets will not be habitable. However, there are arguments that such planets could support life (Kasting 1996, Heath *et al.* 1999).

Kasting *et al.* (1993) compute the likely CHZs for ELPS associated with two different main-sequence stars for comparison with the Earth. The Sun is a G2V star, with an effective photospheric temperature (T_{eff}) of ~5700 K and, from Wien's Law ($\lambda_{max}/\mu m = 2,898/T_{eff}$), a peak energy output at 0.508 μm. This is contrasted with an F0V star ($T_{eff} = 7200$, $\lambda_{max} = 0.403$ μm) and an M0V star ($T_{eff} = 3700$, $\lambda_{max} = 0.783$ μm). Table I shows these data, together with the mass and luminosity

TABLE I

Stellar Properties and Radiation Fluxes at the Inner and Outer Limits of the CHZ[a]

Stellar type	T_{eff} (K)	λ_{max}[b] (μm)	λ_{max}[c] (μm)	$M/M_{(sun)}$	$L/L_{(sun)}$	S_{in}[d] (S_{sun})	S_{out}	r_{in}[e] (AU)	r_{out}
M0V	3700	0.7832	0.9919	0.5	0.06	1.00	0.46	0.25	0.36
G2V	5700	0.5084	0.6439	1.0	1.0	1.10	0.53	0.95	1.37
F0V	7200	0.4025	0.5097	1.3	4.3	1.25	0.61	1.85	2.70

[a] From Kasting *et al.* (1993).
[b] Wavelength of maximum energy flux $[F(\lambda)]$ at T_{eff}.
[c] Wavelength of maximum photon flux $[N(\lambda)]$ at T_{eff}.
[d] Stellar flux relative to present solar constant (1360 W m^{-2}, 0.24–4.5 μm) at the inner and outer limits of the CHZ.
[e] Distance of planet from parent star at the inner and outer limits of the CHZ.

relative to the Sun, and the relative energy inputs at the top of the atmosphere of a planet at the inner and outer limits of the CHZ (corresponding to "water loss" and "CO_2 condensation" respectively) relative to the present solar constant of the Sun (1360 W m^{-2}, 0.24–4.5 μm). Since photosynthesis depends on the number of photons in the photosynthetically active range rather than their energy we also tabulated the wavelengths of maximum photon flux for the three stellar types. Finally, Table I lists the computed orbital distances (AU) for the inner and outer limits of the CHZ for the Earth and the ELPs orbiting the two other stars, computed from the stellar luminosities and the inverse square law. We shall later use these estimates in considering the potential for photosynthesis. However, we note that the inner and outer limits of the CHZ are defined by a climate model in which the main uncertainty is the role of clouds and its effect on the planetary albedo.

Evolution of life by the chemolithotrophic route could have occurred on an ELP in the CHZ in the manner indicated earlier in our consideration of evolution of life on Earth. Evolution deep in the sea at hydrothermal vents would mean that high UV flux incident on the planetary atmosphere, especially for F0 stars among those cited in Table I, would not damage UV-absorbing essential molecules in the early living organisms. This is because the organisms are protected by hundreds or thousands of metres of UV-absorbing water even in the absence of O_2 (and hence O_3) in the atmosphere to absorb the damaging UV-B (and UV-C) shorter wavelengths of UV.

In assessing the potentially damaging role of UV radiation we must be aware that UV emission has two components, both of which vary with stellar age. The photospheric UV component depends on the stellar surface temperature and increases only slowly over the stellar lifetime (Gough 1981); it is appreciable for F stars but relatively weak for the cooler G, K, and M stars. For these latter stars, the UV emission comes mainly from the second UV component, the active chromosphere whose energy derives from dynamo-generated magnetic activity. The energy source for the dynamo is thought to be stellar rotation, which slowly declines with age, and hence the chromospheric UV is

also though to decline with age (Ayres *et al*. 1996, Ayres 1997, Simon 1999).

The means of energy transformation on an ELP need not necessarily involve the detailed mechanisms used on Earth, although redox reactions are essential. Regardless of the mechanistic details of the evolution of chemolithotrophy, an Earth-like planet would be subject to similar overall energetic constraints on the extent of chemilithotrophic primary productivity to those mentioned earlier for the Hadean/early Archaean chemolithotrophic primary producers on Earth, i.e., to about 0.1% of the present photosynthetic primary productivity (see the preceding and Jakosky and Shock 1998).

As on Earth in the late Hadean and Archaean, so at the corresponding stage on an ELP, there would be a large unfilled niche for the catalysed use of light energy to permit CO_2 reduction using weak reductants at rates higher than can be achieved by a chemolithotrophic mechanism.

Ultimately, as on Earth, even the very weak reductants dissolved in water would be used up, since regeneration of the reduced form by regeneration from the oxidised form using "respiratory" reactions oxidising organic carbon back to CO_2 would be incomplete because particulate organic carbon can be sedimented and thus spatially separated from the oxidant (see also Walker 1987). This imbalance sets up the scene on the ELP, as on Earth, for the evolution of O_2-producing photosynthesis with water as reductant.

These arguments suggest that the evolution of O_2-producing photosynthesis is very likely on an ELP. We now consider whether the magnitude of such photolithotrophy is likely to yield sufficient O_2 accumulation in the atmosphere of an ELP to yield enough O_3 in the stratosphere to be potentially detectable for our Solar System and to act as a UV-B and UV-C screen (Lovelock 1975, Cockell 2000) but also to produce a potentially detectable (from our Solar System) quantity of photosynthetic pigments.

A determinant of gross O_2 production in photosynthesis is the incident photon flux density, the fraction of the incident photons which are absorbed, the wavelength range over which photosynthesis is possible, and the number of photons needed to reduce one molecule of CO_2 to carbohydrate or to evolve one molecule of O_2. The two latter factors are closely related, since the energetics of CO_2 reduction and O_2 evolution require two photons at 700–730 nm, three photons at 1050–1095 nm, or four photons at 1400–1460 nm (Hill and Bendall 1960, Hill and Rich 1983, Heath *et al*. 1999). Thus, the greater the long-wavelength limit for photosynthesis, the larger the number of photons needed to fix each CO_2 and evolve each O_2. The quantity of photosynthetic pigment per unit area determines the fraction of incident radiation absorbed, with a decreasing increment of photons absorbed for each doubling of pigment per unit area. The quantity of pigment per unit area is *inter alia* not only a function of the availability of photons to energize synthesis of the pigments but also a function of the availability of nutrients needed to produce the pigments and the associated catalysts (C, N, P, S, Mg, Fe, Mn, Cu, Zn, etc.) and of the size of the proteinaceous (or anal-

ogous) catalysts needed to perform catalysis (Maynard Smith and Szathmáry 1997).

Within the constraints indicated, photosynthetic rates on Earth are limited by resource supply and incident flux density. With sufficient nutrients, and hence sufficient pigment per unit area to absorb almost all of the incident photons, the lower limit on photon flux density at which gross photosynthesis can occur is set by unavoidable back reactions and, for almost 100% photon absorption and a two photons per electron mechanism, it is some 20 nmole photon m^{-2} s^{-1} (Raven *et al*. 2000).

For a four photons per electron mechanism on an ELP the lower limit of 20 nmol photon m^{-2} s^{-1} (Raven *et al*. 2000) would be 40 nmol photon m^{-2} s^{-1}. It is not clear if the more complex mechanisms inherent in a four-photon mechanism necessitates more energy loss by unavoidable back reactions. Furthermore, the requirement for four rather than two photochemical reactions means that irradiation-limited rates of photosynthesis for a mechanism using four photons per electron would only be half that of a mechanism with two photochemical reactions, other things being equal. Finally, a greater number of photochemical reactions implies a more complicated mechanism, where the use of more catalytic macromolecules per redox sequence from water to CO_2 could constrain the rate of radiation-saturated photosynthesis (Raven 1984a,b, 1987). We note that the maximal wavelength for the four-photon mechanism is up to 1500 nm, which is still well beyond the wavelength of maximum energy flux of an M0 star (783 nm; see Table I); the T_{eff} for a star with a λ_{max} of 1460 nm is only 1930 K.

The upper limit of photon flux density at which photosynthesis can occur on Earth is set by the availability of nonphoton resources used in constructing and using the photosynthetic apparatus and by the occurrence of photodamage at high photon flux densities (Raven 1984a, 1989, 1994, Long *et al*. 1994, Anderson *et al*. 1997, Maule *et al*. 1995, Maule and Andrews 1996). These data suggest that some plants on Earth could grow at a photon flux density of 6000–9000 μmol photon m^{-2} s^{-1}, despite the maximum natural photon flux density (400–700 nm) on Earth being 2000 μmol photon m^{-2} s^{-1}. We suggest that photosynthetic primary production can occur on land on an ELP with 10,000 μmol photon m^{-2} s^{-1}; aquatic habitats permit the screening of supra-optimal irradiance by water, provided the water is deep enough (Falkowski and Raven 1997).

For the application of these considerations on the potential for photosynthesis on an ELP, we deal with an ELP located at the inner edge of the habitable zone. Full details of the calculation are given in the Appendix. In Fig. 1 we show the flux of photons absorbed by land plants at the surface of a cloud-free ELP orbiting at the inner edge of the habitable zone for different parent stars: F0V (1.85 AU), G0V (1.02 AU), G2V (0.95 AU), K0V (0.67 AU), and M0V (0.25 AU). The dependence of photosynthesis on photon flux rather than energy flux and the decreasing atmospheric attenuation with increasing wavelength provides a bias in favour of cooler stars, but the F0V star still provides the best parent star environment for an ELP. Integration across
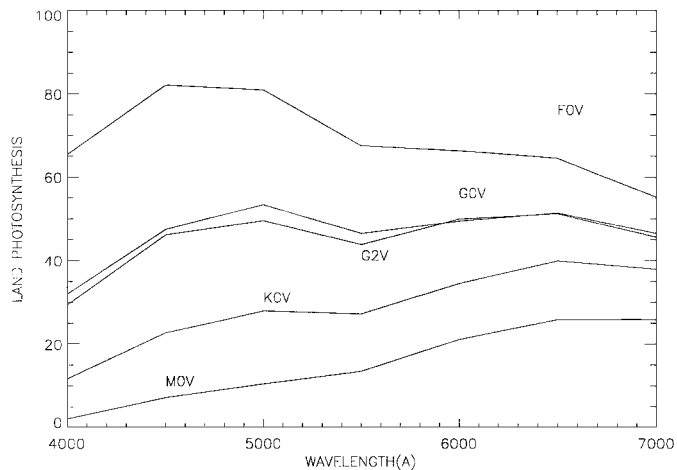
FIG. 1. Flux of photons absorbed by land plants (units of 10^{17} photons m^{-2} s^{-1} nm^{-1}) at the surface of a cloud-free ELP (direct light from parent star only) for an ELP at the inner edge of the star's habitable zone for five types of main-sequence star.

the PAR yields the flux of photosynthetically productive photons (Table A5 in the Appendix). In Fig. 2 the flux of photons observed by marine algae at 10 m depth has been calculated assuming deep ocean seawater transmission, which varies from 97% at the blue peak of chlorophyll (450 nm) to 0.3% at the red peak ($\sim$700 nm); the integrated flux of photosynthetically active photons is listed in Table A8. In this case the blue bias favours the hotter F0V star and this bias would increase with an increase in the fraction of the ELP covered in oceans.

We now tackle the question of clouds. In the Appendix we use the empirical relations between (a) the flux of direct plus
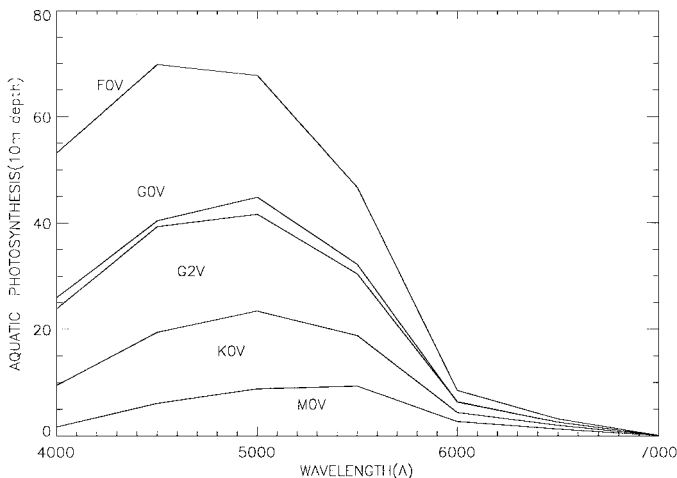

FIG. 2. Flux of photons absorbed by algae (units of 10^{17} photons m^{-2} s^{-1} nm^{-1}) at 10 m ocean depth on a cloud-free planet (direct light from the parent star only) for an ELP at the inner edge of the star's habitable zone for five types of main-sequence star.

diffuse (sky) solar radiation and (b) the cloud cover measured at meteorological stations across the globe, plus global cloud cover statistics, to infer the global value of the PAR in terms of G(clear) the global surface flux of PAR incident on a cloud-free Earth. In Section A.2 of the Appendix we estimate an annual time average of $G = 0.67$ G(clear), but note that this value is slightly uncertain; this value contrasts with that for a completely overcast Earth of 0.25 G(clear).

Clearly we have no way of estimating the cloud cover on an ELP and so we need to calculate models for the global photosynthetic productivity for all possible values of the cloud cover, as well as for values for the fraction, h, of the planet covered in land as opposed to oceans.

Using the former approach we use Eq. (A5) (in the Appendix), which gives the global photosynthetic productivity, p (in units of molecules of O_2 generated globally per second), in terms of the fraction of the planet covered in land (h) and oceans $(1 - h)$ for three values of the fraction of global cloud cover, f. Values of p are tabulated in Table A9 for five types of star from F0V to M0V and illustrated in Fig. 3 for F0V, G2V, and M0V stars. For given values of f and h the productivity p is greatest for the hottest F0V stars and least for the coolest M0V stars. Nevertheless, a given level of O_2 productivity can be attained from a variety of cloud and land fraction values on different parent stars.

Returning to the question of whether a three- or four-photon mechanism might have evolved on ELPs orbiting the cooler K or M stars we note that the achieved rate of photosynthesis could be as little as two-thirds or half that for the terrestrial two-photon mechanism. An example is an M0V ELP ($h = 1.0$) for which the assumed range of PAR is 600–1050 nm and with a three-photon mechanism of photosynthesis. We assume that the pigments absorb the fraction of photons tabulated in Table A3 but at wavelengths of 600 nm (0.95), 675 nm (0.94), etc. The integrated flux between 600 and 1050 nm PAR yields 14.4 instead of 4.63 for the two-photon mechanisms (in units of 10^{20} photon m^{-2} s^{-1}; see Table A5). In applying formula (A3) to obtain global photosynthetic productivity (Table A9) allowance must be made for the 12 rather than 8 photons needed to generate one molecule of O_2. Nevertheless, this brings the cloud-free ELP value of 77 (two-photon mechanism) to 160 (three-photon mechanism) (in units of 10^{30} O_2 molecules s^{-1}) for an M0V parent star. This advantage could turn into a disadvantage for a planet largely covered in oceans because of the attenuation by seawater at wavelengths beyond about 600 nm.

The implicit assumptions about the possible wavelength range over which photosynthetic pigments absorb photons deserve rather more attention. We have seen that photosynthesis on Earth involves chlorin pigments with two absorption peaks, the Soret band in the blue region of the spectrum ($\sim$430 nm) and the Q_y band in the red ($\sim$670–680 nm). Regardless of whether the photons are harvested by the Soret Band (second excited singlet) or the Q_y band (first excited singlet) the energy used in photochemistry is that of the Q_y band with a longer lifetime of electronic
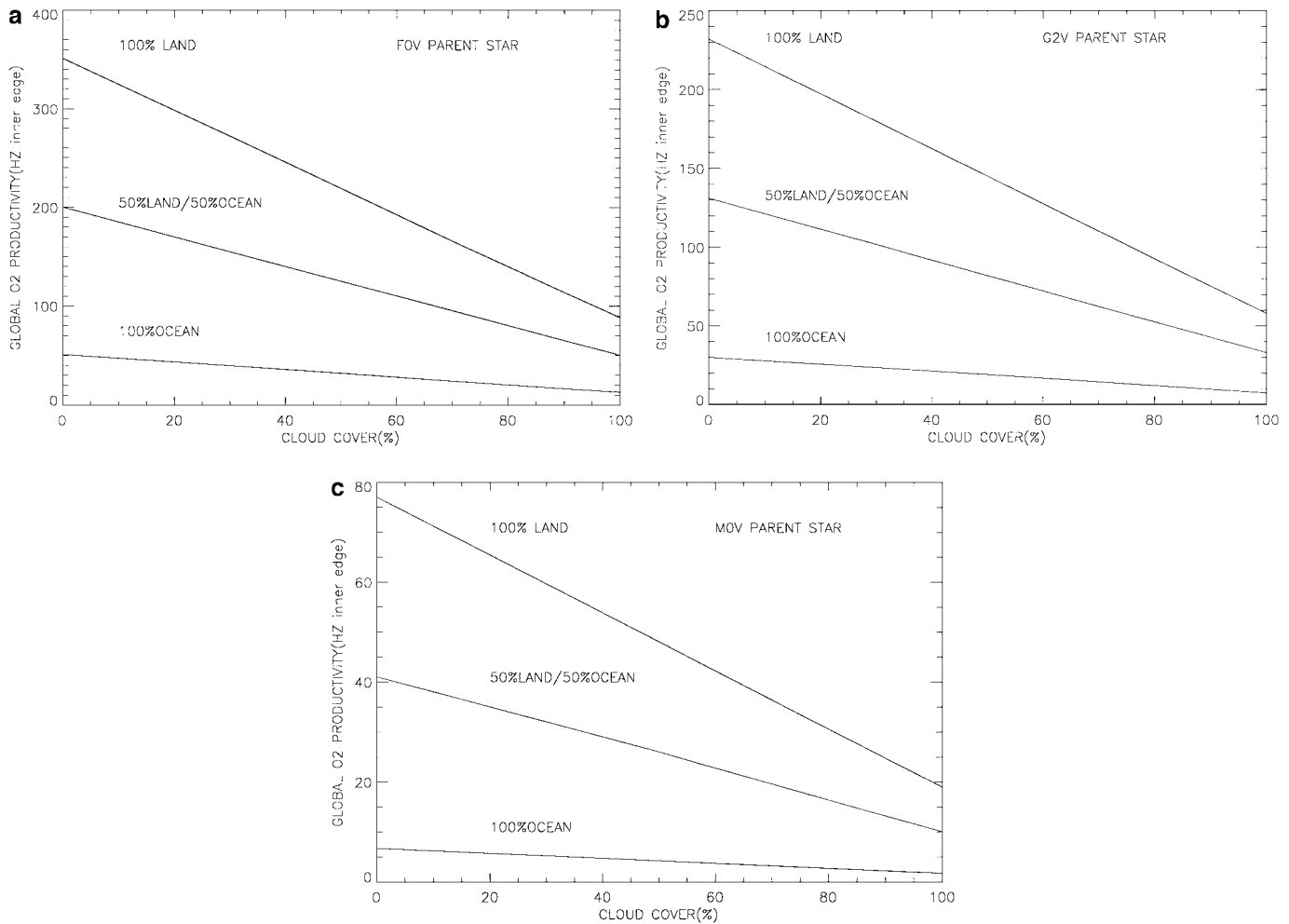
FIG. 3. Global photosynthetic productivity, P, of molecular oxygen (units of 10^{30} molecules s^{-1}) for an ELP at the inner edge of the habitable zone, as a function of the fractional cloud cover, f, and for various fractions of the ELP covered by land and ocean for three types of parent star: (a) F0V, (b) G2V, and (c) M0V.

excitation, increasing the chance of productive photochemistry leading to stable redox products. In the context of evolution, the early occurrence of photosynthesis under the UV screen of liquid water flow would bias the incoming radiation hitting the ocean surface to the shorter visible wavelengths and the longer wavelengths of UV-A (320–400 nm) by the time a deep-growing photosynthetic organism is reached. Even with greater UV absorption relative to absorption at longer wavelengths in the early ocean due to the presence of Fe^{2+} in anoxic waters (Olson and Piersen 1986, Garcia-Pichel 1998) there would still be an emphasis on shorter wavelengths of visible radiation at the depths at which UV-B has been screened out to nonlethal levels. This would favour the evolution of pigments which have absorption in the blue region. If the pigments only absorbed in the blue, then the depth at which photosynthesis could occur in oceans in the CHZ of an ELP associated with an M0 star is restricted since the blue (and, perhaps, UV) emission from such stars is relatively small. The occurrence of photosynthesis at shallower depths or

on land after the production of an atmospheric UV screen on such a planet would be maximized if the pigments were also active at longer wavelengths, a requirement met by chlorin pigments. We note that the evolution of photosynthesis at depth in the ocean would not have precognition of the wavelength range to which organisms would be exposed in shallow water or on land. While a chlorin pigment using only its Soret band for absorption would not have an energetic requirement to use more than two photons per electron for O$_2$-evolving photosynthesis, very significant changes to the photosynthetic apparatus would be required if more photons per electron are to be used to permit use of infrared photons and thus use the full wavelength range on the planetary surface. It is evolutionarily relatively easy to cause large *in vivo* shifts to longer wavelengths for the Q$_y$ band (e.g., to between 760 and 900 nm in photosynthetic bacteria); altering the number of photoreactions is less readily envisioned. For F0 parent stars, the chlorin pigments used on Earth would be appropriate for UV screening at depth in the ocean (e.g., in

early evolution) as well as later for life near the ocean surface or on land on an oxic ELP. The greater depth of ocean needed to screen out the higher UV flux from an F0 star would be permitted by a chlorin pigment due to the higher blue radiation flux from the F0 star as a fraction of its higher output.

Attempting now to integrate the various evolutionary and astronomical threads to see what could be the constraints on photosynthesis by ELPs, we deal first with the inner limit of the CHZ. For Earth, orbiting our (G2V) Sun, at the inner limit (Table I) the flux would have 1.10 times the photon input on the Earth at the moment. This would not threaten the occurrence of photosynthesis due to photoinhibition even on a planet with a lower atmospheric albedo than the present Earth, nor would the occurrence of photosynthesis be threatened by screening by any plausible atmospheric albedo. For a cloud-free ELP orbiting an F0V star, the photon flux at the inner limit is greater but by less than a fraction of 2 than that on the present Earth (see Fig. 1), although with more blue and UV-B and less red and infrared. Even with a higher albedo (Kasting *et al.* 1993) such a star would permit global photosynthesis at a rate not much greater ($\sim$20%) than for the present Earth (Table A9), albeit with a higher UV flux and hence the need for UV screening by compounds produced by the organism. Kasting *et al.* (1997) discuss the UV flux from an F2V star and suggest that the 200–300 nm UV flux on a climatically habitable O_2-free planet would be 5–40 times that for the primitive Earth. Kasting *et al.* (1997) also point out that the evolution of photosynthetic life on such planets could (as on Earth) involve living under water, forming mats, and developing intra- and extracellular UV-protection mechanisms. Another important point made by Kasting *et al.* (1997) is that once O_2 (from photosynthesis) has accumulated, the high UV flux below 200 nm which is incident on the top of the atmosphere of a ELP orbiting an F2V star would produce an O_3 layer twice as thick as on Earth for the same atmospheric O_2 partial pressure. This would serve to reduce the UV flux incident on the surface of an ELP orbiting an F2V star to less than the value of 5–40 times the value incident on the primitive Earth.

For M0V parent stars we have already suggested that, because of the longer wavelength of radiation from such stars, it is possible that a three-or four-photon mechanism might bring the photosynthetic rate closer to that on the present Earth, even granted that absorption by atmospheric CO_2 and H_2O vapour diminishes the potential for (especially land surface) photosynthesis at very long wavelengths. A second effect of the longer wavelength of radiation is that the (probably) lower UV flux from such a later-type star relative to the flux of longer wavelength radiation means that the early evolution of life before any O_2 accumulation in the atmosphere would be less threatened by high UV flux than in the other cases considered here. A counterargument by Sheldon (quoted by Kasting *et al.* 1997) suggests a minimal UV screening by O_3 once O_2 has accumulated on an ELP in the CHZ of a late-type star, due to the very strong depletion of the shortest UV wavelengths which convert O_2 to O_3. However, detailed calculations do not bear out this expectation,

and nonlinearities in the feedback effects in O_3 photochemistry mean that the ozone layer is only 18% thinner than that of Earth with the same O_2 partial pressure (Kasting *et al.* 1997). Thus, the lower flux of longer wavelength UV relative to that of wavelengths beyond 400 nm from the late-type star is not offset by the even lower flux of short-wavelength UV reducing the O_3 screening effect in the oxygenated atmosphere. We conclude that the ratio of UV-B to flux above 400 nm is lower on an ELP orbiting a late-type planet than it is on Earth.

Turning to the possible rates of net O_2 accumulation on ELPs, and the steady-state O_2 levels, we summarize the possible rates of photosynthesis for planets with 50% ocean and 50% land in Table A9. An ELP at the outer edge of the CHZ intercepts only half as many photons as a similar sized ELP at the inner edge. For an ELP within the HZ, the range relative to the present Earth is as small as 5 : 1 for an M0V ELP at the outer edge of the HZ. If the global cloud cover, f, were an entirely free parameter then the range could be significantly greater. These values suggest that the O_2-producing primary productivity of ELPs of the type considered here are, in the CHZ, between about one-fifth and twice that on the present Earth. To translate the capacity for photosynthetic O_2 production into net O_2 accumulation in the atmosphere, we need to consider the processes which consume O_2 on the ELPs. An ELP with one-fifth the rate of primary production on the present Earth (e.g., an outer limit M0V) might have an O_2 accumulation rate which is much lower than one-fifth that of the Earth. One reason is that biological processes other than photosynthesis determine O_2 accumulation; these are organic C burial processes rather than reoxidation and interconversions of Fe^{2+} and Fe^{3+} and S^{2-}, S^0, and SO_4^{2-}. To the extent that organic C burial is limited by P (and other nutrient) inputs to the biosphere, if weathering is limited by photosynthetic activity (Algeo and Scheckler 1998) then organic C burial may comprise a smaller fraction of primary production than on Earth. However, if phosphorus supply is not constrained in this way, then a greater fraction of primary production may be buried on an outer limit M0V ELP. However, the abiological processes consuming O_2, i.e., reductant supply from the effectively infinite reductant stores deeper in the crust by volcanic and hydrothermal activities (Berner and Petsch 1998, Paytan *et al.* 1998), are likely to consume a greater fraction of photosynthetic O_2 when primary productivity is lower.

This comparison involves planets very similar in size to Earth. Larger planets with tectonic activity, which are continually bringing fresh reductant from the larger volume (proportional to radius cubed) of crust to the area (proportional to radius squared) of planetary surface, are predicted to have a larger ratio of O_2 consumption by inorganic reducing agents to photosynthetic O_2 production than on smaller tectonically active planets (McKay 1998).

More massive, tectonically active ELPs near the outer limit of the CHZ with relatively low (radiation-limited) rates of photosynthesis might produce O_2 from photosynthesis at so low a rate as to not exceed the rate at which O_2 is consumed by inorganic

reductants (see McKay 1998). This would mean that even an ELP with long-term ($\geq 2 \times 10^9$ years) occurrence of photosynthetic organisms generating O_2 might not have enough O_2 in its atmosphere, either to provide sufficient O_3 as a UV screen or for this low level of O_3 to be remotely detected. Further, if the parent star is both cool (say M0V) and old, so that it is rotating slowly, then the combined photospheric and chromospheric UV emission could be too low to provide a UV screen, irrespective of the rate of O_2 generation, as a result of the low level of UV flux. Paradoxically, this means that, despite the minimal UV flux incident on the upper atmosphere, sufficient UV could reach the ELP surface to limit the photosynthetic generation of O_2 to organisms in the oceans. These considerations mean that the accumulation of significant O_2 on an outer limit ELP may take several billion years. Thus, most ELPs on which life developed would become oxygenated within a few billion years, but some outer limit planets might not. Accordingly, the spectroscopic O_2 (via O_3) assay seems like a reasonable but not all-encompassing one for life on ELPs.

Finally, what are the prospects for sensing photosynthetic pigments and O_3 (and hence O_2) on ELPs? The Earth intercepts 4.6×10^{-10} of the solar radiation and thus, if viewed from a distance of 10 parsecs, the Earth, with its visual albedo of about 0.3, would contribute just one in 7.3×10^9 of the photons that might be detected in an alien astronomer's telescope aperture focussed on the Sun and inner planets. If this astronomer had an instrument capable of completely separating the solar and terrestrial optical photons entering it—the Earth being just 0.1 arcsec from the Sun—it would only take 20 min to accumulate 100 terrestrial photons in a 50 bandpass at 550 nm with a collecting area equivalent to that of a 5-m telescope with 50% throughput and thus to allow this observer to start searching for the reflection discontinuity at 700 nm associated with photosynthetic pigments. However, the technical difficulties of achieving this discrimination between the optical photons from the ELP and its parent star are unlikely to be overcome soon. While an 8-m telescope with wavefront control of $\lambda/5000 \sim 0.1$ nm and an advanced coronagraph could in principle achieve this (Malbet *et al*. 1995, Woolf and Angel 1998), this approach is unlikely to be realised in practice in time for the Next Generation Space Telescope. Almost certainly the first step will be to detect mid-IR ELP radiation using a nulling interferometer in space (see, e.g., Woolf and Angel (1998) and the Terrestrial Planet Finder Report by Beichman *et al*. (1999)) and to search for mid-IR absorption in the ELP atmosphere by O_3 (as well as CO_2, H_2O, and CH_4) as evidence for O_2-generating photosynthesis. The next step would be to infer seasonal changes in the level of photosynthesis which could be associated with the relative ocean and land coverage in the two hemispheres. Such changes in the atmospheric O_3 parameters measured on a pale blue dot would perhaps be globally smoothed out and difficult to interpret for a number of factors including seasonal cloud cover and O_3/O_2 chemistry. It remains to be seen what further progress could be achieved with a single pale blue dot to work with, until the advent of optical

imaging and spectroscopy with NASA's Planet Imager would finally permit direct evidence for the presence of photosynthetic pigments.

In a similar vein it is worth recalling our earlier suggestion that for cooler parent stars, especially M0V stars, the evolutionary pressure for the photosynthetic pigments to match the spectral energy distribution (SED) of the star could in principle lead to three- or four-photon systems that would have a long-wavelength limit to the pigment absorption system at 1050 or 1400 nm; the corresponding reflection discontinuity for such ELPs would be such that observations across this boundary would be needed. Ironically if this has in fact happened in some cases there would probably be no great improvement in the star/planet brightness contrast ratio at these longer wavelengths (if the SED and pigments remained well matched) and hence in the ability to search for evidence of pigments, unless the evolutionary process was slow or ineffective.

APPENDIX: CALCULATION OF PHOTOSYNTHETIC PRODUCTIVITY

The rate at which O_2 is generated on a remote ELP depends on the rate at which photons are absorbed by the pigments of photosynthetic organisms at the planetary surface. To calculate this rate we need to know the flux, $F(\lambda)$, of radiation from the parent star at the top of the ELP atmosphere that falls in the photosynthetically active range (PAR); the fraction, $j(\lambda)$, of this radiation that reaches the planetary surface; and the fraction, $g(\lambda)$, of these photons that are absorbed and are used in the photosynthetic process.

A.1. Photon Flux at the Top of the ELP Atmosphere

Given the distance of the ELP from its parent star and the type of star, we know $F(\lambda)$ but have no a priori knowledge of either $j(\lambda)$ or $g(\lambda)$. In the simplest case (Section IV) we have assumed that the planet is identical to the Earth in terms of its atmospheric $j(\lambda)$, the properties of the pigments defined by $g(\lambda)$, and its planetary diameter. The energy flux of a star with a V magnitude of zero [λ(eff) = 550 nm] is tabulated by Allen (1973) for main-sequence spectral types A0V, F0V, G0V, K0V, and M0V. Since photosynthetic productivity depends on the photon flux and not on the energy flux, we need to calculate the photon flux, which at the top of the ELP atmosphere will depend on the absolute V magnitude of the class of parent star and the actual distance between ELP and parent star. We adopt the values of the absolute V magnitude tabulated by Lang (1992) and use them to determine the distance, d, at which each class of star would have magnitude V = 0. The photon flux for an ELP 1 AU distant from its parent star is then obtained by multiplying by $[d/(1\ \text{AU})]^2$ and is tabulated in Table A1.

A.2. Net Photon Flux at the ELP Surface

The net flux of photons arriving at any given location of the Earth's surface comprises the direct sunlight after transmission through the atmosphere and the diffuse component scattered in the atmosphere (Fleagle and Businger 1963). Both of these components depend on the cloud cover at this location. To estimate the global PAR flux, G, integrated over the planet we need to be able to assess the global cloud cover, which varies with time of year and latitude, as does the type, vertical extent, and opacity of "cloud," and how the diffuse and direct components differ at clear and cloudy sky sites. This information comes from both satellite studies and surface observations from meteorological stations but is not well determined.

Measurements of the spectral reflectivity of the Earth viewed towards the nadir from the GOME (Global Ozone Monitoring Experiment) spectrometer across the PAR range (Burrows *et al*. 1999) show that for 100% cloud cover the albedo

TABLE A1
Photon Flux[a] at the Top of the Atmosphere of an ELP 1 AU from Its Parent Star

λ (nm)	A0V	F0V	G0V	K0V	M0V
350	1474	155	25.9	—	—
400	4001	374	55.6	8.74	0.219
450	3346	409	71.9	14.9	0.658
500	2831	378	75.6	16.9	0.890
550	2363	357	74.8	18.8	1.30
600	1942	314	71.1	21.4	1.82
800	1193	226	62.2	22.7	2.37
1000	889	177	51.9	19.9	2.15

[a] Units of 10^{17} photons m^{-2} s^{-1} nm^{-1}.

TABLE A2
Direct Component of Photon Flux[a] at the Surface of a Cloud-Free Planet 1 AU from Its Parent Star (Earth-like Atmosphere)

λ (nm)	A0V	F0V	G0V	G2V	K0V	M0V
350	693	73.0	12.2	16.6	—	—
400	2520	236	35.0	27.9	5.51	0.138
450	2440	299	52.5	44.4	10.9	0.480
500	2240	298	59.7	48.1	13.4	0.703
550	1960	296	62.1	50.7	15.6	1.08
600	1630	264	59.8	52.3	18.0	1.53
650[b]	1460	245	59.4	51.3	19.9	1.80
700[b]	1320	231	59.0	50.2	20.7	1.97
800	1120	212	58.5	45.9	21.3	2.23
1000	854	169	49.8	36.4	19.1	2.78

[a] Units of 10^{17} photons m^{-2} s^{-1} nm^{-1}.
[b] Interpolated values.

is between 55 and 60% and approximately wavelength independent; the type of cloud is not known and so this cannot be assumed to be a typical value for cloud albedo; however, the neutral colour of the reflected light is probably typical and related to the scattering of light by water droplets in the clouds. The diffuse light of the sky seen below the clouds is also approximately neutral in colour relative to sunlight; i.e., it has the same colour as the direct sunlight (see, e.g., Bonhomme 1993) since scattering dominates and little light is truly absorbed in the clouds in the 400–700 nm range. As expected the GOME spectrum above a clear part of the Atlantic Ocean (which has low surface albedo) is dominated by Rayleigh scattering from the clear atmosphere.

The dependence of the flux, Q, of diffuse plus direct solar radiation at surface stations on the cloud cover has been examined by a number of authors, and these studies have been discussed by Coulson (1975). Probably the most useful relation is Ångström's formula (1924),

$$Q = Q(\text{clear}) [k + (1 - k)(n/N)], \qquad (A1)$$

where Q is the flux of diffuse plus direct solar radiation measured on a horizontal surface during a day when n/N is the fraction of the day with bright sunshine, and Q(clear) is the value on a cloudless day ($n/N = 1$); k is a constant that depends on the type of cloud and varies from about 0.25 for stratus cloud to 0.82 for cirrus (Haurwitz 1948; see also Table 4.1 of Coulson 1975). This is measured over a wider wavelength range than that of the PAR, but it should provide a satisfactory estimate for our purposes. Global cloud cover statistics based on surface observations at meteorological stations for the period June 1995 to May 1996 as a function of latitude (Breon, private communication, 1998) yield an estimate of the global average of 13% clear sky, 65% broken cloud component, and 22% overcast. As a working model we adopt ($k = 0.25$, $n/N = 0$) for the overcast component and ($k = 0.75$, $n/N = 0$) for the broken cloud component, leading to global values G (as opposed to Q values at surface stations) of

$$G = G(\text{clear}) [0.13(1.0) + 0.65(0.75) + 0.22(0.25)] = 0.67 \, G(\text{clear}), \quad (A2)$$

where G(clear) is the global value of the PAR flux incident at the surface of a cloudless Earth. This compares to 0.25 G(clear) for a totally cloud-covered Earth. Note that the appropriate k value to be used here is somewhat uncertain. Perhaps just as valid would be to assume that the broken cloud component was half clear and half overcast ($k = 0.25$), which would yield 0.59 G(clear); i.e., overall a value G/G(clear) $= 0.63 \pm 0.04$ is more realistic. In the preceding we have assumed that these three components have the same SED, i.e., solar, as modified by the transmission of the atmosphere. This is true for the direct components in all three cases but less so for the diffuse (scattered) components for clear and broken cloud. For the clear sky case about 20% of the Q(clear) value comes from the diffuse, Rayleigh scattered component, which is hence

bluer than solar but somewhat less in the broken cloud case. However, given the overall uncertainties we have ignored these spectral differences, which are relatively small, and assumed that all components have the same SED. The zenith sea level transmission, T, of the Earth's clear atmosphere (see Allen 1973) across the photosynthetically active range (400–700 nm) is due mainly to molecular scattering and shows a redward bias with T ranging from 63% at 400 nm to 91% at 700 nm. The wavelength dependence of the photon flux reaching the surface of a cloud-free planet whose atmospheric transmission is identical to that of the Earth is given in Table A2 for a planet which is assumed to be 1 AU from its parent star. The quantity tabulated is the direct photon flux: the global value, G(clear), including the diffuse sky contribution is assumed to be 1.25 times the value listed in Table A2.

A.3. Photosynthetic Rate at the Planetary Surface (Land)

Having determined the photon flux at the surface of a planet identical to the Earth at 1 AU from its parent star we can now estimate the photosynthetic rate for a planet within the habitable zone of its parent star, assuming that the photosynthetic pigments are also identical to those on Earth. To evolve one O_2 molecule requires eight PAR photons, which are absorbed by the pigments: the fraction of photons absorbed by the leaf of a typical land plant is listed in Table A3 (taken from Gates 1980).

Thus photosynthesis due to "typical" plants such as the oleander (*Nerium oleander*) would generate O_2 molecules globally at the photosynthetic rate, $p(\lambda)$ (units of O_2 molecules/s), where

$$p(\text{land}) = 1.25 \times (1/8) \times hBq_1 \times (G/G(\text{clear})) \times T_1 \times [A2 \cdot A3] \quad (A3)$$

and where the factor 1.25 allows for the diffuse sky radiation; (1/8) accounts for the number of absorbed photons needed to generate one molecule of O_2; B is the cross-sectional area of the solid planet, h is the fraction of the Earth

TABLE A3
Fraction of Photons Absorbed by the Photosynthetic Pigments in a Leaf of Oleander (*Nerium oleander*)

λ (nm)	400	450	500	550	600	650	700
Fraction absorbed	0.95	0.94	0.93	0.78	0.86	0.90	0.82

TABLE A4
Direct Component of Flux of Photons Absorbed by Land Plants[a] at the Surface of a Cloud-Free Planet for Unit Air Mass for an ELP 1 AU from Its Parent Star

λ (nm)	A0V	F0V	G0V	G2V	K0V	M0V
400	2394	224	33.3	26.5	5.23	0.131
450	2294	281	49.4	41.7	10.2	0.451
500	2083	277	55.5	44.7	12.5	0.654
550	1529	231	48.4	39.5	12.2	0.842
600	1402	227	51.4	45.0	15.5	1.316
650[b]	1314	221	53.5	46.2	17.9	1.620
700[b]	1082	189	48.4	41.2	17.0	1.615

[a] Units of 10^{17} photons m^{-2} s^{-1} nm^{-1}.
[b] Interpolated values.

where surface photosynthesis as opposed to aquatic photosynthesis takes place; q_1 is the effective fraction of that surface covered in such plants (allowing for the density of plants and nutrient availability); G/G(clear) allows for cloud cover; T_1 is an atmospheric transmission factor that takes account of the fact that Table A2 is calculated for a zenith air mass; and [A2 · A3], the product of Tables A2 and A3, is proportional to the flux of photons absorbed by the plant pigments. For planets identical in all respects to the Earth all the factors save [A2 · A3] would be the same: [A2 · A3] is listed in Table A4.

Atmospheric models by Kasting et al. (1993; hereafter KWR) indicate that an ELP will not be able to retain its surface water due to catastrophic water loss within a certain distance of its parent star, namely the inner edge of the habitable zone. Using the figures in Table A4, and for the moment ignoring the other factors in Eq. (A3), we list in Table A5 the integrated flux of photosynthetically productive photons across the PAR range (400–700 nm) for ELPs at the inner edge of the HZ for the various parent stars. As expected this shows that for a cloudless planet the photosynthetic productivity is much greater for the hotter F0V stars than for the cooler K0V and M0V stars.

The models of KWR, which were developed primarily to deduce the location of the planetary habitable zones, also lead to values of planetary albedo that differ for planets orbiting different types of star. These albedos are higher (and the PAR flux available at the surface is hence lower) for planets orbiting F stars and the albedos are lower for planets orbiting M stars: this results from the differing amount of Rayleigh scattering in the ELP atmospheres (which is greatest where there is the most incident blue parent starlight) and from the greater atmospheric absorption by water vapour (see Appendix B of Kasting 1988) at near-infrared as opposed to visible wavelengths. However, the KWR models do not allow for changes in cloud cover: instead the presence of a fixed

TABLE A5
Integrated Flux of Photosynthetically Productive Photons at the Inner Edge of the HZ

Spectral type	Stellar temperature (K)	Inner edge of HZ (distance, AU)	Absorbed photon flux (10^{20} photons m^{-2} s^{-1})
F0V	7200	1.85	21.2
G0V	6030	1.02	14.4
G2V	5860	0.95	14.0
K0V	5250	0.67	8.89
M0V	3850	0.25	4.63[a]

[a] 14.4 for photosynthesis using 3 instead of 2 photons/electron.

amount of cloud is implicity included by assuming a high surface albedo (0.22), which allows their climate model to be consistent with the current mean global terrestrial surface temperature at 288 K. As KWR acknowledge, their assumption implies a fixed amount of cloud cover with no cloud feedback. There are still very considerable difficulties in putting clouds (at various optical thicknesses and atmospheric heights) into realistic climate models. While the KWR models provide a reliable guide to the location of the habitable zones, they cannot be used to assess the effects of variable cloud cover and some other approach is needed.

To deduce the flux of PAR radiation received at the surface of an ELP we clearly need to estimate the cloud cover factor G/G(clear). For the Earth we can consider a simple approach, namely the use of the global version of Eq. (A1),

$$Q/Q(\text{clear}) = k + (1-k)(n/N) \rightarrow G/G(\text{clear}) = (1-f) + kf, \quad \text{(A1)}$$

where f is the fraction of global cloud cover. The fraction of the day with bright sunshine, n/N, transforms to the fraction of the planet with no cloud, $(1-f)$, for which $n/N = 1$ and hence $G/G(\text{clear}) = 1$; and the cloudy fraction of the day, for which $n/N = 0$, transforms to the cloudy fraction of the planet and hence $G/G(\text{clear}) = k$. For simplicity we assume either all clear or all overcast (stratus: $k = 0.25$) conditions: hence $G/G(\text{clear}) = 1 - f + 0.25\,f = 1 - 0.75\,f$. In the case of the Earth we could in principle produce a more sophisticated estimate of G/G(clear) and attempt to apply it to other ELPs, since we have detailed knowledge of how the visible solar radiation incident at the top of the Earth's atmosphere is distributed: namely 31% is reflected into space (global albedo, A), 23% is absorbed by the atmosphere and clouds, and 46% is absorbed at the ground (see, e.g., Schlesinger 1997). Of the 31% albedo, about 6% is attributable to scattering at the surface and by the atmosphere, and 25% is attributable to cloud: recent studies of the global albedo by means of Earthshine observations (Goode et al. 2001) have noted that the albedo varies over time by a few percent with the expected correlation between albedo and cloud cover being confirmed. One difficulty in trying to infer useful facts about the G/G(clear) for the PAR radiation from these values is that the albedo measurements are generally made not only at visible wavelengths but also at wavelengths beyond the PAR range (>700 nm) where atmospheric absorption plays an important role, so that the figures used here on absorption by clouds and atmosphere (23%) and at the surface (46%) do not necessarily apply in the PAR range.

Any attempt to model the relation between albedo and cloud cover, even for Earth, is at best a difficult task because it involves a very wide range of albedos of natural surfaces and of various cloud types (see, e.g., Miranova 1973) and because the radiation transfer processes involved are complex. A simple relation between albedo and cloud cover for the Earth might be written

$$A = (R_1)f + (R_2)(1-f),$$

where the cloud reflectivity is R_1 and the reflection into space by air and surface is R_2. Using the cloud cover statistics of F. M. Breon (private communication, 1998) mentioned earlier we have $f = 0.55$, which, given $(R_1)f = 0.25$ and $(R_2)(1-f) = 0.6$, yields $R_1(\text{cloud}) = 0.45$ and $R_2(\text{surface}) = 0.13$. This implies that the radiation retained by the Earth, $1 - A = 0.87 - 0.32f$, is 73%, 69%, and 66% for $f = 45\%$, 55%, and 65%. These figures are not too far from the corresponding numbers based on $G/G(\text{clear}) = 1 - 0.75f$, namely 66%, 59%, and 51%, and the differences between the two sets of numbers perhaps represents a realistic estimate of their errors. It is clear that in estimating the effect on cloud cover for other ELPs we have no choice but to use the equation (A1) above for G/G(clear) for all ELPs.

A.4. Photosynthetic Rate in the Planetary Oceans

In the case of the Earth 71% of the planet is covered by oceans and a considerable amount of photosynthesis takes place in the surface layers of the oceans. However, the photosynthetic productivity of the oceans is relatively poor compared to the land: each year the oceans fix about 40 G tonnes of carbon and the

TABLE A6
Aquatic Photosynthesis Loss Factor

λ (nm)	Seawater transmission(s) at 10 m depth	Fraction, c, of photons absorbed by the green macroalga *Codium fragile*	Aquatic loss factor (0.9sc)
400	0.94	0.91	0.77
450	0.97	0.92	0.80
500	0.94	0.92	0.78
550	0.70	0.86	0.54
600	0.14	0.85	0.11
650	0.055	0.90	0.045
700	0.0025	0.73	0.0016

land fixes about 60 G tonnes (Raven and Falkowski 1999). Photosynthesis in coastal waters is relatively efficient and produces in each year about 2 to 3 G tonnes of carbon, but the bulk of the photosynthesis occurs in the oceans beyond the continental shelf. Light loss as the PAR radiation enters the ocean depends on the wave height and the solar zenith distance: we shall assume an overall light loss of 10% across the PAR range. The depth at which the great majority of PAR photons are absorbed varies greatly and it is difficult to estimate the effective ocean depth at which the bulk of photosynthesis takes place: we adopt a depth of 10 m.

The transmission, s, of seawater at 10 m depth, which we list in Table A6, is much higher in the blue than in the red, which favours the hotter stars. In this table we also list the fraction, c, of PAR photons absorbed by the photosynthetic pigments in the marine green alga *Codium fragile*, which is typical of marine algae (Lüning and Dring 1985). Multiplication of these factors together with the factor of 0.9 for light loss at the surface yields the aquatic loss factor (0.9sc) to be applied to the photon flux in Table A2 to give (in Table A7) the aquatic equivalent of Table A4.

The equation for oceans analogous to Eq. (A3) is

$$p(\text{ocean}) = 1.25 \times (1/8) \times [(1-h)Bq_2 \times (G/G(\text{clear}))$$
$$\times T_1 \times T_2 \times [\text{A2.A6}]], \qquad (A4)$$

where $1-h$ is the fraction of the Earth where oceanic photosynthesis could potentially be taking place; q_2 is the effective fraction of this area where it is taking place (allowing for density of algae, etc. and nutrient availability); T_2 is analogous to the term T_1 for atmospheric transmission; and [A2.A6] is the product of Tables A2 and A6 (listed in Table A7).

TABLE A7
Direct Component of Flux of Photons Absorbed by Algae[a] at 10 m Ocean Depth on a Cloud-Free Planet for Unit Air mass for an ELP 1 AU from Its Parent Star

λ (nm)	A0V	F0V	G0V	G2V	K0V	M0V
400	1940	182	27.0	21.5	4.24	.106
450	1952	239	42.0	35.5	8.72	0.384
500	1747	232	46.6	37.5	10.5	0.548
550	1058	160	33.5	27.4	8.42	0.583
600	179	29.0	6.58	5.75	1.98	0.168
650	65.7	11.0	2.67	2.31	0.90	0.081
700	2.1	0.4	0.09	0.08	0.03	0.003

[a] Units of 10^{17} photons m^{-2} s^{-1} nm^{-1}.

TABLE A8
Integrated Flux of Photosynthetically Productive Photons at the Inner Edge of the Habitable Zone at 10 m Ocean Depth in the ELP Ocean (Cloud-Free Planet)

Spectral type	Inner edge of HZ (distance, AU)	Absorbed photon flux (10^{20} photons m^{-2} s^{-1})
F0V	1.85	11.4
G0V	1.02	7.2
G2V (Sun)	0.95	6.8
K0V	0.67	3.8
M0V	0.25	1.5

The integrated flux over the PAR wavelength range of Eqs. (A3) (land, see Table A5) and (A4) (ocean, see Table A8), i.e., the number of O$_2$ molecules/s generated globally, is

$$P = P(\text{land}) + P(\text{ocean})$$
$$= 0.156B \times T_1 \times (G/G(\text{clear}))[hq_1[\text{A5}] + (1-h)q_2T_2 \times [\text{A8}]]. \quad (A5)$$

A.5. Selected Planetary Models

Table A9 lists the global photosynthetic productivity, P, for a representative set of planet models. For simplicity we assume all the model ELPs have the same collecting area, B, as the Earth (i.e., 1.28×10^{18} cm^2) and the same value of T_1. We ignore the slight dependence of T_1 on stellar spectral type and adopt $T_1 = 0.83$ based on a mean air mass of 2.0. For the efficiency factors we adopt $q_1 = 0.01$ and $q_2 \times T_2 = 0.27q_1$ based on the relative terrestrial productivity of land and oceans. We assume, as before, that $G/G(\text{clear}) = 1.0$ (0.25) for the cloud-free (cloud-covered) parts of the planet respectively.

TABLE A9
Global Photosynthetic Productivity of O$_2$[a] at Inner Edge of Habitable Zone

Spectral type	r (AU)	$h = 1.0$ (land only)	0.5	0.0 (ocean only)
		I. Cloud-free planet		
F0V	1.85	351	200	51
G0V	1.02	239	136	32
G2V	0.95	232	131	30
K0V	0.67	147	81	17
M0V	0.25	77	41	6.7
		II. 50% cloud cover, 50% cloud-free		
F0V	1.85	219	125	32
G0V	1.02	149	85	20
G2V	0.95	145	82	19
K0V	0.67	92	51	11
M0V	0.25	48	26	4.2
		III. 100% cloud cover		
F0V	1.85	88	50	13
G0V	1.02	60	34	8.0
G2V	0.95	58	33	7.5
K0V	0.67	37	20	4.3
M0V	0.25	19	10	1.7

[a] Units of 10^{30} molecules s^{-1}.

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