

Special Paper

Spectral Signatures of Photosynthesis. I. Review of Earth Organisms

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ABSTRACT

Why do plants reflect in the green and have a “red edge” in the red, and should extrasolar photosynthesis be the same? We provide (1) a brief review of how photosynthesis works, (2) an overview of the diversity of photosynthetic organisms, their light harvesting systems, and environmental ranges, (3) a synthesis of photosynthetic surface spectral signatures, and (4) evolutionary rationales for photosynthetic surface reflectance spectra with regard to utilization of photon energy and the planetary light environment. We found the “near-infrared (NIR) end” of the red edge to trend from blue-shifted to reddest for (in order) snow algae, temperate algae, lichens, mosses, aquatic plants, and finally terrestrial vascular plants. The red edge is weak or sloping in lichens. Purple bacteria exhibit possibly a sloping edge in the NIR. More studies are needed on pigment–protein complexes, membrane composition, and measurements of bacteria before firm conclusions can be drawn about the role of the NIR reflectance. Pigment absorbance features are strongly correlated with features of atmospheric spectral transmittance: P680 in Photosystem II with the peak surface incident photon flux density at ~685 nm, just before an oxygen band at 687.5 nm; the NIR end of the red edge with water absorbance bands and the oxygen A-band at 761 nm; and bacteriochlorophyll reaction center wavelengths with local maxima in atmospheric and water transmittance spectra. Given the surface incident photon flux density spectrum and resonance transfer in light harvesting, we propose some rules with regard to where photosynthetic pigments will peak in absorbance: (1) the wavelength of peak incident photon flux; (2) the longest available wavelength for core antenna or reaction center pigments; and (3) the shortest wavelengths within an atmospheric window for accessory pigments. That plants absorb less green light may not be an inefficient legacy of evolutionary history, but may actually satisfy the above criteria. **Key Words:** Photosynthesis—Photosynthetic pigments—Leaf spectral reflectance—Oxygenic photosynthesis—Anoxygenic photosynthesis—Atmospheric radiative transfer—Chlorophyll—Bacteriochlorophyll—Red edge—Radiation spectrum—Photosynthetically active radiation—Light harvesting—Review—Virtual Planetary Laboratory. *Astrobiology* 7(1), 222–251.

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1. INTRODUCTION

THE UTILIZATION OF THE SUN'S LIGHT ENERGY by photosynthetic organisms provides the foundation for virtually all life on Earth, with the annual amount of carbon fixed from CO₂ into organic form by land plants and by ocean phytoplankton being each approximately ~45–60 Pg-C/year (Cramer *et al.*, 1999, 2001), or 6–8% of the atmospheric carbon content (Reeburgh, 1997). The selective utilization of light energy results in two well-known spectral signatures exhibited in land plants: the “green bump,” due to lower absorbance of green light by chlorophyll (Chl); and the “red edge,” characterized by absorbance in the red by Chl strongly contrasting with reflectance in the near-infrared (NIR) due to refraction between leaf mesophyll cell walls and air spaces in the leaf. The red edge is so different spectrally from other matter that it has been measured by satellites to identify vegetation cover (Tucker, 1976; Grant, 1987; Sagan *et al.*, 1993) and estimate plant productivity (Potter *et al.*, 1993).

We seek to address and extend the age-old question: why are plants green? More precisely, what is the functional role of different features of a photosynthetic organism's reflectance spectrum? Although it is fairly well understood how pigments absorb and how cells scatter light, it is not yet settled as to why photosynthetic pigments absorb at those particular wavelengths. Finally, how ubiquitous is the NIR reflectance among photosynthetic organisms, and how does it serve the organism?

Photosynthetic spectral reflectance signatures are a result of both molecular constraints on biochemical processes and environmental pressures for adaptation. In this review, we attempt to synthesize spectral characteristics across the full range of Earth's photosynthesizers, covering the following:

1. A brief review of how photosynthesis works.
2. An overview of the diversity of photosynthetic organisms, their light harvesting systems, and environmental ranges.
3. A synthesis of photosynthetic surface spectral signatures.
4. An exploration of evolutionary rationales for photosynthetic surface reflectance spectra, including the Earth's chemical history, energy requirements for conversion of photon energy

to chemical energy, and the planetary light environment.

We conclude with some hypotheses about why photosynthetic pigments favor their particular wavelengths, and whether alternative whole-organism reflectance spectra could be possible. As this review is motivated by speculation about photosynthesis on Earth-like planets in other solar systems, much of the discussion is placed in this context and geared toward the diverse multidisciplinary astrobiology audience. This review should also be useful to specialists in Earth remote sensing, photosynthesis, and plant physiology.

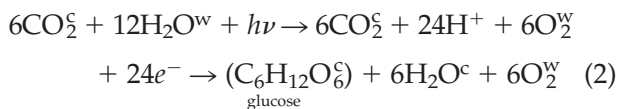
2. BACKGROUND: BASIC PROCESSES OF PHOTOSYNTHESIS, INPUTS, AND OUTPUTS

Photosynthesis efficiently converts light energy to electrochemical energy for oxidation–reduction (“redox”) reactions. The excitation of light harvesting pigments by a photon of light causes an electron to be transferred along biochemical pathways that lead to the reduction of CO₂. The electron is replaced by one extracted from the reductant. The basic stoichiometry of photosynthesis is:



where H₂A is a reducing substrate such as H₂O or H₂S, and $h\nu$ is the energy per photon, where h is Planck's constant, and ν is the frequency of the photon or the speed of light divided by the photon wavelength.

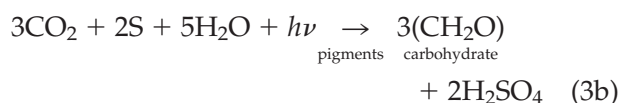
When the reductant is water, then we have oxygenic photosynthesis:



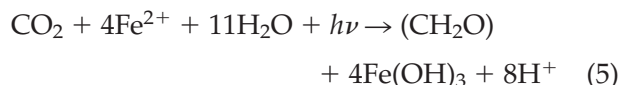
where the superscripts c and w denote the oxygen from carbon dioxide versus that from water, respectively. Four photons are required for each O₂ evolved (one photon for each bond in two water molecules), and four photons are needed to reduce two molecules of the coenzyme NADP⁺

eventually to reduce one CO₂. Thus, a minimum of eight photons total are required both to evolve one O₂ and to fix carbon from one CO₂. Six cycles are required to obtain the six carbons to make the six-carbon sugar, glucose. More than eight photons are generally required [experiments have shown up to about 12 photons (Govindjee, 1999)] because some are unsuccessful, and some in addition are used in the processes of cyclic photophosphorylation [which occurs in Photosystem I (PS I) generation of ATP, described later (Joliot and Joliot, 2002; Munkage *et al.*, 2004)] and nitrogen assimilation (Foyer and Noctor, 2002). The mechanisms by which these processes are achieved are highly complex, and the reader is referred to details in textbooks and recent findings (Voet *et al.*, 1999; Ke, 2001; Ferreira *et al.*, 2004; Green and Parson, 2004; Wydrzynski and Satoh, 2005; Golbeck, 2006).

Photosynthesis may use reductants other than water, such as H₂S, H₂, and Fe²⁺, in anoxygenic photosynthesis. When the reductant is H₂S, then elemental sulfur is produced instead of oxygen, and that sulfur may be further oxidized to sulfate (Van Gemerden and Mas, 1995):



When the reductant is H₂ (Vignais *et al.*, 1985) or Fe²⁺ (Ehrenreich and Widdel, 1994; Jiao *et al.*, 2005), the reactions are:



(In Eq. 5, actually HCO₃⁻ and not CO₂ is directly used, though it could come from CO₂ dissolved in water or from dissolution of some other carbonate source; the Fe²⁺ could be from dissolution of, *e.g.*, FeCO₃.)

The quantum requirement in all these cases is also 8 to 12 photons per carbon fixed. In summary, the inputs to photosynthesis are light energy, a carbon source, and a reductant. The direct products are carbohydrates and can be oxygen, elemental sulfur, water, and other oxidized forms

of the reductant. Soil nutrients are also necessary inputs, described in more detail below.

3. RANGE OF PHOTOSYNTHETIC ORGANISMS, HABITATS, PIGMENTS, METABOLISMS, AND ENVIRONMENTAL LIMITS

Photosynthetic organisms are adapted to occupy different niches according to both physical (light, temperature, moisture) and chemical resource (electron donors, carbon sources, nutrients) requirements. In addition, their environmental ranges may be controlled by the presence of competing or grazing organisms. The range of photosynthetic organisms is shown in Table 1, which lists the approximate time of their appearance on Earth, the significant features that distinguish them metabolically and spectrally, their relative abundance and productivity over the Earth, habitats, their pigment types, reaction center (RC) types, electron donors, growth mode and growth form, carbon sources, and metabolic products.

3.1. Emergence of photosynthetic organisms on Earth

Photosynthesis arose fairly early in the history of the Earth. One theory about the origin of photosynthesis is that it began as a fortuitous adaptation of primitive pigments for infrared thermotaxis of chemolithotrophic bacteria in hydrothermal ocean vents [early Archean, possibly 3.8 Ga ago (Nisbet *et al.*, 1995)]. Thus, with these organisms being less dependent on the heat of the hydrothermal vents, their habitats gradually expanded to shallower waters where solar light could be utilized (Nisbet and Fowler, 1999; Des Marais, 2000). It is also possible that photosynthesis arose first in shallow waters and, before there was oxygenic photosynthesis to provide an ozone shield, ultraviolet (UV) screening proteins led to the transfer of excitation energy to the porphyrin (Mulkidjanian and Junge, 1997). The evolution of ocean chemistry could have played a major role in the evolution of Chl (Mauzerall, 1976; Blankenship and Hartman, 1998; Dismukes, 2001; Dasgupta *et al.*, 2004). Blankenship and Hartman (1998) proposed that hydrogen peroxide (H₂O₂) could have been a transitional electron donor on the oxygen-poor early Earth. Liang *et*

al. (2006) posited that the necessary high H_2O_2 in the oceans could have occurred after a "Snowball Earth" event (low-latitude glaciation), around 2.3 Ga, because of storage of H_2O_2 in ice and its subsequent release into the oceans upon deglaciation. Protocyanobacteria early in the Archean may have utilized $\text{Fe}(\text{OH})^+$ as a reductant (Olson, 2006). Dismukes *et al.* (2001) proposed that bicarbonate could have been a transitional reductant before water in the Archean ocean and reacted with manganese (II) to form Mn-bicarbonate clusters as precursors to the $(\text{Mn})_4$ core of the oxygen-evolving complex; the redox potentials are such that green sulfur bacteria would have been the early hosts of these clusters prior to the evolution of cyanobacteria. Allen and Martin (2007) provide a nice review of these ideas of the origins of oxygenic photosynthesis.

The fossil record seems to support that the early photosynthesizers were anoxygenic purple bacteria and green sulfur bacteria that used reducing substrates other than water, such as H_2 and H_2S (Olson, 2006). Anoxic environments allowed these organisms to thrive, since oxygen is damaging to bacteriochlorophylls (BChls). By the mid- to late Archean (3.5–3.6 Ga ago) or as late as 2.3 Ga ago in the Early Proterozoic, oxygenic cyanobacterial mats had formed in the shallower waters. Endosymbiosis of cyanobacteria and early animal protists gave rise to the plastids of algae, with these plastids being the photosynthesizing organelle (Larkum and Vesik, 2003). The algae were, thus, the first eukaryotic photosynthesizers and occur in both single-cell and multicellular forms (*e.g.*, kelp). Red algae appeared around 1.2 Ga ago. Eukaryotic green algae did not appear until as late as 750 Myr ago. These photosynthetic organisms were protected under water from UV radiation until O_2 and, hence, O_3 built up in the atmosphere. With the rise of atmospheric O_2 , the anoxygenic ancestors lost their competitive advantage to organisms that could withstand and respire O_2 (or so one may interpret). Land plants are believed to be descended from a single branch of the green algae (Larkum and Vesik, 2003). The first land plants, with the nonvascular Bryophyta (mosses and liverworts) being the earliest, did not occur until 460 Myr ago, after which the abundance of plant life exploded, reaching a first peak of productivity by the end of the Devonian 360 Myr ago (Bambach, 1999; Carroll, 2001; Igamberdiev and Lea, 2006). Further complexity continued to arise through

the emergence of flowering plants (144 Myr ago), and more water-efficient photosynthetic pathways came about through anatomical and enzymatic changes. In crassulacean acid metabolism (CAM) photosynthesis, which arose 70–55 Myr ago, CO_2 is stored in an intermediate at night; during the day, stomates remain closed to prevent water loss, and the intermediate is broken down for CO_2 to enter the Calvin-Benson cycle. In C4 photosynthesis, which arose 20–35 Myr ago, CO_2 is similarly concentrated in an intermediate that is transported to an internal bundle of cells that allow stomates to draw in atmospheric CO_2 through a smaller aperture (Sage, 2001).

So it seems natural for organisms to evolve to capture stellar energy, and Earth's example shows that they continue to get better at it, especially once they emerge from the water. Earlier organisms are more diverse in their photosystems, while later organisms are more complex in their morphological properties. Note that not all photosynthesizers are autotrophs (fix CO_2), but many of the bacteria are heterotrophs that utilize organic carbon, though some may use both inorganic and organic carbon. The halobacteria do not perform actual photosynthesis, in that no electron transfer is performed, but their pigment bacteriorhodopsin drives a proton pump for heterotrophic assimilation of organic carbon. Of greatest interest to us are those photosynthesizers that are autotrophic and can fix CO_2 directly, as these are the primary producers and the foundation for life on Earth. We survey next their photosystems and environmental constraints.

3.2. Light harvesting

Photosynthetic organisms have intricate photosystems that coordinate (1) the spectral selection of light energy and (2) the abstraction of electrons from electron donors. These photosystems are composed of three main components. The (1) peripheral or outer antenna complex transfers light energy to (2) the core or inner antenna. These two together are known as the light harvesting complex (LHC). The core antenna is also an integral part of the third component, (3) the RC complex, where light energy is finally converted to chemical energy in charge separation (*e.g.*, with H_2O , other electron donors, enzymes) (Ke, 2001).

The photon utilized must be of sufficient energy to generate a voltage potential difference that is great enough to oxidize the reductant as

TABLE 1. RANGE OF PHOTOTROPHIC ORGANISMS ON EARTH

Apperred	Taxon	Growth mode/form	Cell wall	RC	Pigments	e-donor	C source*	Products	Niche	Global abundance (Pg-C)	Gross productivity (Pg-C/yr)
3.8 Ga	BACTERIA	Unicellular								0.06	51
	Anoxygenic										
	Green non-sulfur filamentous	Anoxygenic photoorganoheterotroph		Type II	BChl a/c/ and or d/e +car	sulfide	Organic C, CO ₂	S	Dense microbial mats in hot springs often in association with cyanobacteria, thermophilic; flocculent surface layer in alkaline springs; <i>Chloroflexus</i> : max -70°C, cannot fix N, resistant to UV		
	Aerobic chemooorganoheterotroph	Anoxygenic photolithoautotroph	Type I	BChl a + c/d/e +car	sulfide, reduced S, H ₂ , Fe	Organic C, acetate, propionate, pyruvate; CO ₂	sulfate	Non-thermal aquatic ecosystems, hot springs, max 55-56°C (<i>Chlorobium tepidum</i>)			
3.6-2.3 Ga	Purple bacteria	Aerobic and anoxygenic heterotrophs and anoxygenic autotroph		Type II	BChl a/b +car	inorg&orgC, S, sulfate, sulfide, sulfite, H ₂ , Fe	Organic C, CO ₂	S, sulfate, CO ₂	Fresh and marine waters, eutropic marine, hot springs, anoxic aquatic sediments; maximum > 50°C (<i>Chromatium tepidum</i>)		
	Heliobacteria	Anoxygenic photoorganoheterotroph		Type I	BChl g+car	sulfide, reduced S, sulfate	Pyruvate, ethanol, lactate acetate, butyrate	?	Soil, dry paddy fields, occasionally lakeshore muds, hot springs; resistant to UV, fix N; survive at least to 42°C		
	Halobacteria (not actual photosynthesis)	Aerobic chemoorganoheterotroph	C5 isoprenoid chains attached to glycerol by ether linkages	bacterio-rhodopsin		N/A	Organic C	?	Salt crusts in marine salterns, saline lakes, evaporites, ~4M NaCl		
1.2 Ga	Rhodophytes (red algae)	Eukaryotes, autotrophs, unicellular, multicellular		Type I & II	Chl a/b/c/d +PBS+car	H ₂ O, S	CO ₂	O ₂	Everywhere, -15 to +75°C	?	?
	Chlorophytes (incl. brown algae)	Eukaryotes, autotrophs, unicellular, multicellular	Cellulose, xylan	Type I & II	Chl a + PBS + car	H ₂ O, other?	CO ₂	O ₂	Fresh and marine waters, snow	2	~100
750 Ma	Chlorophytes (green algae)	Eukaryotes, autotrophs, unicellular, multicellular	Cellulose, xylan	Type I & II	Chl a/c/+car				Minimum observed PAR flux 0.01 μmol/m ² /s		
	Lichens	Symbiosis of fungus and cyanobacteria/algae, crustose, squamose, foliose, fruticose	Cellulose		Chl a/b/c +PBS + car				Rock outcrops, vegetation surfaces	?	?

Appeared	Taxon	Growth mode/form	Cell wall	RC	Pigments	e-donor	C source*	Products	Niche	Global abundance (Pg-C)	Gross productivity (Pg-C/ty)
	PLANTS	Leaves, stems, roots	Cellulose, lignin, polysaccharides, protein, water, calcium	Type I & II	Chl a/b/ +car	H ₂ O	CO ₂	O ₂ VOCs	Minimum observed PAR ~3 μmol/m ² /s (0.7 W/m ²)	550-680	~90-120
460 Ma	Bryophytes Mosses Liverworts	Non-vascular <i>Sphagnum</i> , <i>Acrocarpus</i> , <i>Pleurocarpus</i>							Moist land environments		
144 Ma	Vascular plants Aquatic plants C3 pathway Flowering plants	Broadleaf, needleleaf, herbaceous, succulent	No lignin				CO ₂ , HCO ₃ ⁻		Aquatic to desert environments		
70-55 Ma	CAM										
20-35 Ma	C4 pathway										

Ga, billion years ago; Ma, million years ago; Pg-C, petagrams (10¹⁵g) of carbon; RC, reaction center; PBS, phycoobilisomes; car, carotenoids; VOC, volatile organic compound; PAR, photosynthetically active radiation; CAM, crassulacean acid metabolism. *C source related only to the photosynthetic process (disregards carnivorous plants).
 Bacteria compiled by Janet Siefert. Additional carbon sources and electron donors from Overmann and Garcia-Pichel (2000), Decker *et al.* (2005), Blankenship *et al.* (1995), Eraso and Kaplan (2001), and Miller *et al.* (2005). Algae from Larkum and Vesik (2003). Plants from Nobel (1999). Abundance and productivity numbers from Reeburgh (1997) and Cramer *et al.* (1999). Red algae minimum PAR flux from Litter *et al.* (1986). Bacterial abundance and productivity are autotrophic only, primarily marine cyanobacteria, estimated from Whitman *et al.* (1998).

well as afford the electron transfers for reduction of the relevant intermediates (and some enzymes). In plants and all oxygenic photosynthesis, there are two stages of light utilization: (1) in the extraction of electrons from water [using Photosystem II (PS II), peaking in absorbance at 680 nm] to regenerate the next step; and (2) for the reduction of the electron carrier NADP^+ (using PS I, peaking in absorbance at 700 nm), which is then used in the Calvin-Benson cycle and for the synthesis of ATP. This two-step sequence is known as the “Z-scheme” for the zig-zag in redox potential at each step [first proposed by Hill and Bendall (1960); first proven by Duysens *et al.* (1961); see Blankenship and Prince, 1985]. The redox potential is the Gibbs free energy change of a reaction (calculated with the Nernst equation), which may be expressed in volts and is the propensity of an oxidation–reduction reaction to proceed spontaneously in one direction or the reverse; the convention is that hydrogen has a redox potential of 0 at standard conditions and that electrons move spontaneously in the direction of

higher (toward positive) potentials. These thermodynamics determine how much energy may be stored as product, while the kinetics of electron transfer affect light harvesting and the quantum yield. All oxygenic photosynthesizers utilize both PS I and PS II, with water as the reductant. Anoxygenic photosynthesizers utilize only a single photosystem that uses other electron donors, for which equations were given earlier. Figure 1 shows the RC midpoint redox potentials (when concentrations of reductants and oxidants are the same) and excited potentials for the Z-scheme of oxygenic photosynthesis, as well as the electron transport pathways for different classes of bacteria. The Type I and Type II RC categories distinguish the types of electron acceptors used. Only oxygenic photosynthesis is known to utilize two RCs in sequence. For a more detailed overview, the reader is referred to Blankenship (2002).

Photosynthetic pigments are categorized into three chemical groups or “chromophores”: the Chls, carotenoids, and phycobilins. The Chls are the pigments of the RCs and also occur in the core

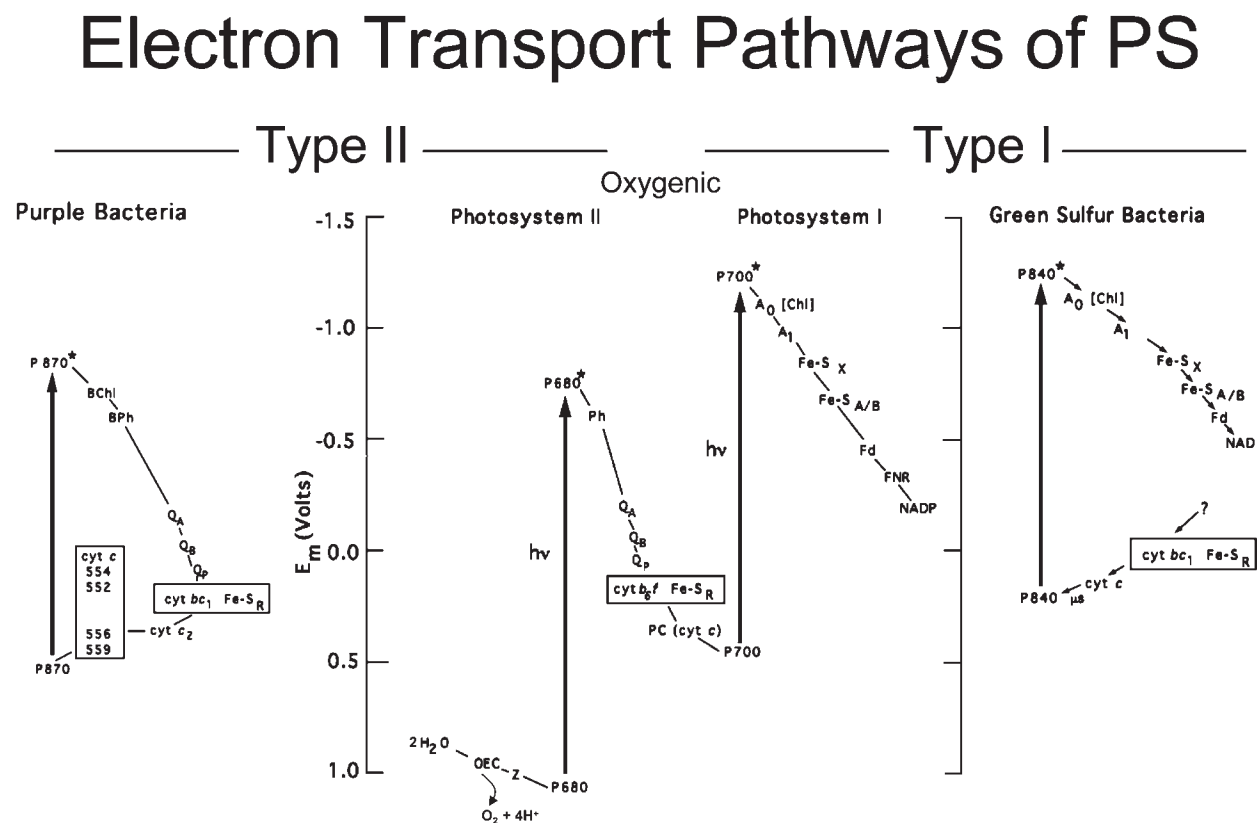


FIG. 1. Electron transport pathways of photosynthesis, with midpoint redox potentials of ground and excited states of the RCs, of biochemical intermediates and reduced products. Shown are photosystems for purple bacteria, green sulfur bacteria, and oxygenic photosynthesis.

antennae and light harvesting antennae (Grimm *et al.*, 2006). Specialized Chls at the RCs serve to “trap” the excitation energy and convert the electronic energy to chemical energy through charge separation. The funneling of energy from the LHCs in all eukaryotes is achieved through a rather remarkable process known as resonance excitation transfer [also known as the Förster mechanism; reviewed by Clegg (2004)], in which a pigment is excited by light at a particular wavelength, and the subsequent de-excitation of the pigment, rather than resulting in a loss of energy to heat or fluorescence, leads to the excitation of another pigment whose energy level overlaps. A series of such excitations and de-excitations creates an “energy cascade” toward longer wavelengths. In all oxygenic eukaryotes, Chl a occurs in the core antenna and acts as the primary donor in the RC; H₂O is the electron donor. Other Chls (Chl b/c/d) provide light harvesting roles, but very recently Chl d, which was discovered in cyanobacteria (Miyashita *et al.*, 1996; Miller *et al.*, 2005), may replace Chl a in the RCs in some cyanobacteria that live in environments with little visible light (Chen *et al.*, 2005; Larkum and Kühl, 2005). Chl d has its major peak absorbance in the NIR at ~720 nm (Manning and Strain, 1943; Larkum and Kühl, 2005), and thus oxygenic photosynthesis is being performed in the NIR! In nonoxygenic bacteria, BChls play the role of primary donor, with a great variety having distinct absorption spectra; a variety of electron donors are possible, including H₂S, H₂, Fe, sulfate, thio-sulfate, sulfite, and organic carbon.

The other pigments as well as additional Chls (particularly Chl b in plants and green algae, and Chl c in diatoms and brown algae) in the LHCs act as “accessory” pigments to help obtain light energy: the carotenoids in the blue and green and the phycobilins (cyanobacteria and red algae) in the green and yellow. The carotenoids in addition serve to protect Chl against photooxidative damage in conditions of high light, high temperature, O₂, and the presence of certain pigments (Nobel, 1999). Oxygen would be toxic to photosynthetic organisms without the presence of carotenoids.

The absorbance spectra of all pigments are influenced by the protein complexes in which they are bound, such that there can be variations in the same type of pigment and the peak absorbances *in vivo* tend to be broadened and shifted compared to those of the pure pigments extracted in

solution (Vasil’ev and Bruce, 2006). For example, Chl a in the PS I RC peaks at 700 nm, whereas in the PS II RC it peaks at 680 nm. We compare *in vivo* pigment spectra (in intact membranes) below.

Figure 2a shows the *in vivo* absorbance spectra of the major pigments found in plants and algae (Chl a, Chl b, and carotenoids; phycobilins exist only in certain algae and cyanobacteria), as well as the spectrum of Chl a fluorescence (Papageorgiou and Govindjee, 2004), together with the incident solar radiation spectrum at the top of the Earth’s atmosphere and at the surface of the Earth after atmospheric filtering. Sources and measurement methods for the pigment spectra are summarized in Appendix A1. The Chl a fluorescence spectrum effectively identifies the upper wavelength limit to absorbance by Chl. The photon flux densities are from models as detailed in the legend of Fig. 2; in addition, measurements from buoys at Hawaii (Dennis Clark, National Oceanic and Atmospheric Administration, personal communication) are plotted to show how varying atmospheric optical depth can affect the incident light spectrum. The atmosphere performs spectral filtering of radiation, with Mie and Rayleigh scattering of light in the bluer wavelengths, and with clear bands of absorption by gases, most importantly O₃, O₂, H₂O vapor, and CO₂, as indicated in Fig. 2a. Plant and algae pigments clearly must have evolved to have their absorbance peaks in atmospheric transmittance windows for radiation and are confined to the visible range, which is commonly considered to be “photosynthetically active radiation” (PAR), 400–700 nm (the tail of the absorbed range extends as far as 730 nm).

Figure 2b shows the *in vivo* absorbance spectra of the BChls with associated carotenoids in intact membranes (sources and measurement method are summarized in Appendix A1). Above these are plotted the transmitted radiation spectrum through 5 cm of pure water as well as through 10 cm of water containing algae [water absorption coefficient from Segelstein (1981), Sogandares and Fry (1997), and Kou *et al.* (1993); for algae absorption coefficient from kelp, see Appendix A2 for explanation of the calculation]. Water is highly transmitting in the visible and highly absorbing in the NIR, as can be seen from the spectrum for pure water at 5 cm depth. A small transmittance window exists, however, in the NIR, peaking at 1,073 nm. Algae and cyanobacteria in

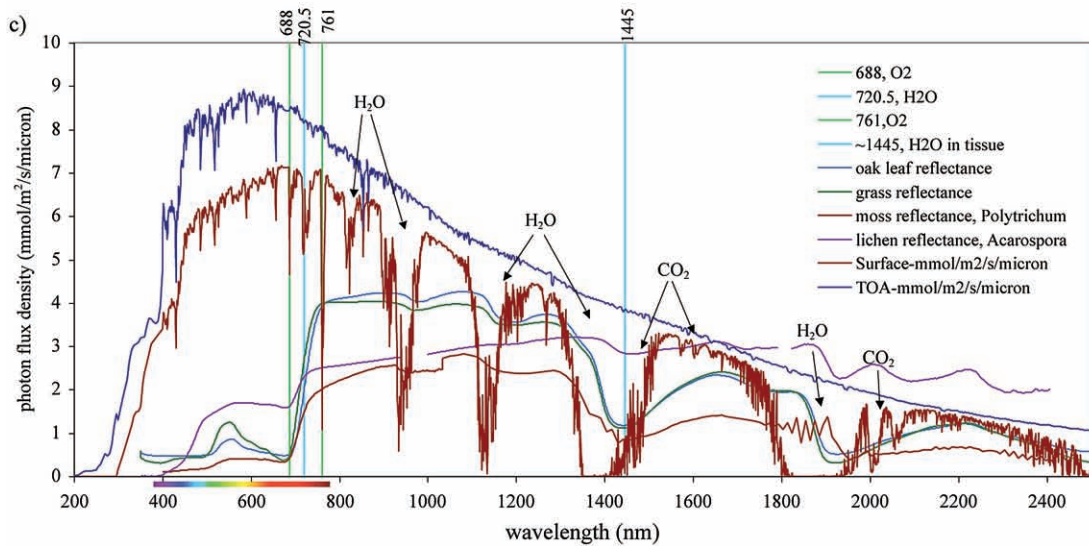
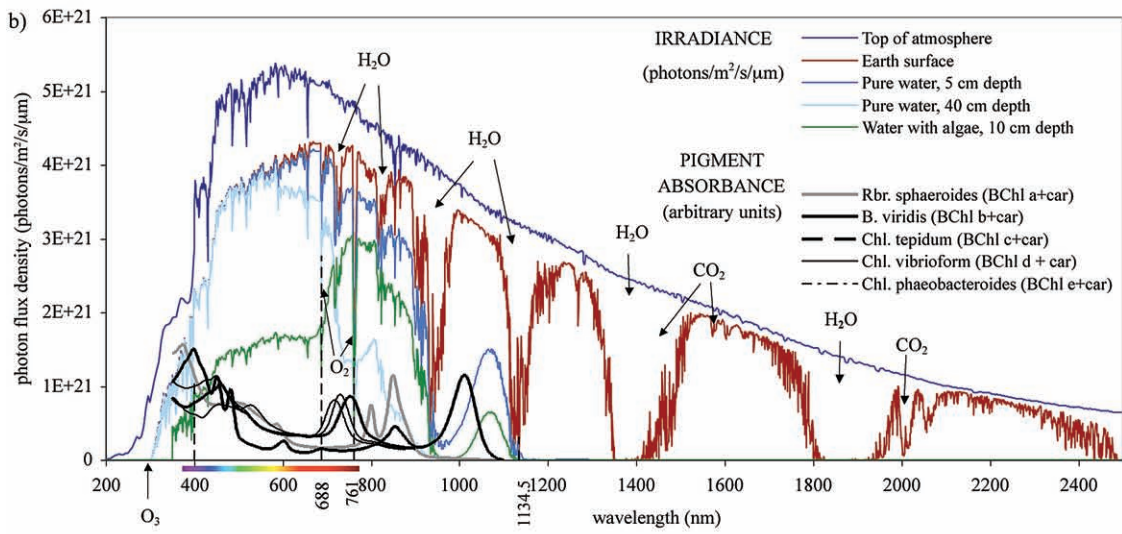
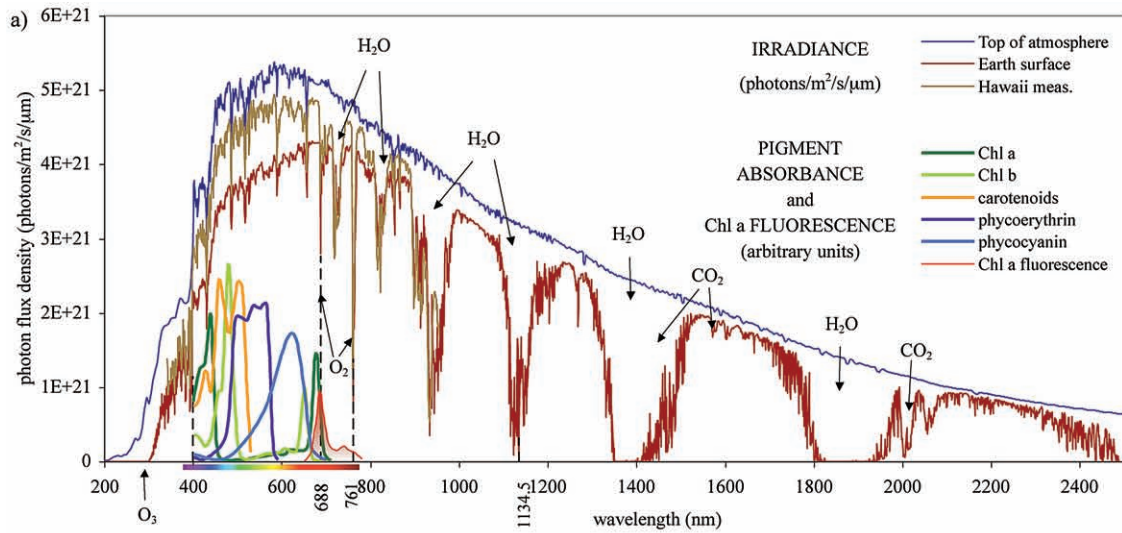
the upper layers of water may strongly attenuate visible light, such that only radiation above about 700 nm may be transmitted to depth and attenuated again by water above 900 nm. The cyanobacterium *Acaryochloris marina*, which uses Chl d at ~715–720 nm instead of Chl a, may be adapted to receive this remaining longer wavelength filtered through overlying organisms. The BChls commonly absorb in the range 700–900 nm. In an extreme case, BChl b in the purple bacterium *Blastochloris viridis* (formerly *Rhodospseudomonas viridis*) can absorb to wavelengths as long as 1,013–1,025 nm (Trissl, 1993; Scheer, 2003). *B. viridis* inhabits murky, anoxic sediments where little visible light penetrates. Its exact peak absorbance is sensitive to temperature, and the range of measurements on lab cultures may, perhaps, not be exactly the same as in the bacterium's native environment. The local peak in water transmittance at 1,073 nm leaves room for speculation that either *B. viridis* has the capability to harvest light at even longer wavelengths, or the wavelength of peak absorbance is limited by exciton transfer kinetics to the RC or thermodynamic constraints.

In addition to the BChls, phototrophic bacteria will also utilize carotenoids, with the ratio between BChl and carotenoids varying with light quality. In Fig. 2b, the absorbance peaks in the blue wavelength range are due to carotenoids. Purple and green sulfur bacteria pigments thus absorb in transmittance windows under water.

Overall, the full range of pigments has been observed to absorb light in the wavelength ranges 330–900 nm and 1,000–1,100 nm (Scheer, 2003). Oxygenic photosynthesis on Earth is limited to photosystems that operate at 400–730 nm, but anoxygenic photosynthesis occurs at wavelengths as long as 1,015–1,020 nm (Trissl, 1993; Scheer, 2003).

To summarize (see Table 1), phototrophic bacteria utilize BChls in their RCs and are the most diverse in their growth modes, with many being heterotrophs and some using sulfide, iron, or hydrogen as their electron donors (Ehrenreich and Widdel, 1994; Eraso and Kaplan, 2001). Among the phototrophic bacteria, only cyanobacteria (formerly known as blue-green algae) are oxygenic. The diversity of pigments of cyanobacteria includes Chl a/b/c/d, phycobilins, and carotenoids, which allows them a wide range of colors and distribution nearly everywhere on Earth, from aquatic environments to desert salt crusts. Where cyanobacteria or algae coexist with fungi in lichens, they can support a level of productivity comparable to vascular plants. All algae utilize Chl a and carotenoids; in addition, green algae use Chl b. Several other algae (*e.g.*, diatoms and brown algae) use different forms of Chl c, and red algae utilize phycobilins instead of Chl b or Chl c. Plants utilize only Chl a, Chl b, and carotenoids but have developed more complex mechanisms to acquire CO₂ and retain water. All photosynthetic organisms have carotenoids.

FIG. 2. (a) Solar spectral photon flux densities at the top of the Earth's atmosphere and at the Earth's surface, and estimated *in vivo* absorption spectra of photosynthetic pigments of plants and algae. Sources: modeled photon flux densities from the following: top-of-the-atmosphere (TOA) irradiance: 150–200 nm, Andrew Lacis, NASA Goddard Institute for Space Studies (GISS); 200–400 nm, Judith Lean (Naval Research Laboratory); 400–2,500 nm, Brian Cairns, NASA GISS. Surface irradiance: 200–400 nm, J. Lean (Lean and Rind, 1998); 400–2,500 nm, Brian Cairns (Cairns *et al.*, 2003). Hawaii buoy measurements were from Dennis Clark (National Oceanic and Atmospheric Administration). Chl a and Chl b absorbance measurements, made by Junzhong Li (Du *et al.*, 1998), *in vitro*, were shifted in wavelengths to match *in vivo* peaks, and absorbances were normalized to between 0 and 1. Carotenoid absorption spectra are estimated *in vivo* absorption spectra in green algae (Govindjee, 1960). Phycoerythrin and phycocyanin absorption spectra are unpublished absorption spectra from Govindjee's laboratory, and from Ke (2001). Chl a fluorescence spectrum, from spinach chloroplasts, is from Govindjee and Yang (1966). Pigments, measurement method, and sources are listed in Appendix A1. (b) Solar spectral photon flux densities at the top of the Earth's atmosphere, at the Earth's surface, at 5 cm depth in pure water, and at 10 cm depth of water with an arbitrary concentration of brown algae; algae and bacteria pigment absorbance spectra. Sources: TOA and surface incident radiation same as (a). Water spectral absorption coefficient: 200–380 nm, Segelstein (1981); 380–640 nm, Sogandares and Fry (1997); 640–2,500 nm, Kou *et al.* (1993). Algae (brown, kelp, *M. pyrifera*) absorption coefficient from reflectance spectrum was measured (in lab, in air) by N.Y. Kiang with an Analytical Spectral Devices FieldSpec spectroradiometer (instrument from the Jet Propulsion Laboratory Airborne Visible/Infrared Imaging Spectrometer Lab). BChl pigment absorbance spectra are all *in vivo* in intact membranes, including carotenoids. BChl a (*R. sphaeroides*) and BChl b (*B. viridis*) spectra are from Richard Cogdell and Andrew Gall. BChl c, d, and e spectra are from green sulfur bacteria (Frigaard *et al.*, 2004). Pigments, measurement method, and sources are listed in Appendix A1. (c) Solar spectral photon flux densities at TOA and at the Earth's surface, with reflectance spectra of terrestrial plants, moss, and lichen (source: Clark *et al.*, 2003), and O₂ and H₂O absorbance lines.



Because the photosystems are tied to the type of electron donor, the photosynthesizer is therefore necessarily restricted to particular resource environment niches. Purple and green sulfur bacteria are restricted to aquatic environments where sulfur (sulfide, sulfate, sulfite, thiosulfate, H_2S) is available as an electron donor, and some of these bacteria require anoxic environments. Cyanobacteria and other photosynthetic bacteria are also known to form mutualistic communities in microbial mats in benthic (Decker *et al.*, 2005) and freshwater aquatic environments (Wiggli *et al.*, 1999), where distinct layering demarcates both light and chemical niches. Exudates and organic carbon from one layer provide the electron source or food source for another, and the lower, anoxic layers utilize sulfide or H_2S for the electron donor. The upper layers of cyanobacteria and algae absorb visible light, such that the lower layers of sulfur bacteria utilize the NIR radiation that transmits through.

Next we will comment briefly on the other environmental constraints on photosynthetic organisms, as these can affect also their spectral properties.

3.3. Climate—water and temperature

Water and temperature are the primary constraints on the distribution, spatially and temporally, of different organisms. For plants, the reader is referred to well-known global surveys of the climate limits of, for example, grasslands, broadleaf temperate deciduous forests, evergreen needleleaf forests, and boreal rainforest, to name some possible categories of many (Holdridge, 1967; Whittaker, 1975; Woodward, 1987; Larcher, 1995). These large-scale classifications show clear correlations between climate and plant form and mixtures of plant communities, such as broadleaf trees in temperate and tropical zones versus needleleaf trees in colder climates. The resulting difference in spectral signatures can be distinguished by satellites (Tucker *et al.*, 1985; Defries and Townshend, 1994). Mosses and liverworts, which lack vascular structure, require very moist and often shaded environments, and do not form large structures. Lichens (symbioses between fungi and algae or cyanobacteria) are limited to environments with moist air but can be highly productive. They are often the first colonizers on rock substrate and can be the dominant source of net primary productivity and a source of food for

animals in some land ecosystems (Ager and Milton, 1987; Rees *et al.*, 2004), in some cases accounting for 70% of the land cover (Solheim *et al.*, 2000). The extreme temperature limits of photosynthetic organisms range as low as -15.7°C , the survival limit for arctic snow algae and arctic ice shelf cyanobacteria (but they require liquid water for growth) (Gorton *et al.*, 2001; Mueller *et al.*, 2005), and as high as $\sim 75^\circ\text{C}$ for bacteria in hot springs (Miller *et al.*, 1998). Meanwhile, the temperature limits for Earth life in general can be as low as -20°C (possibly as low as -196°C for some methanogenic bacteria) (Junge *et al.*, 2006) and possibly as high as 120°C (Kashefi and Lovley, 2003).

3.4. Extreme environments

Photosynthetic bacteria and some algae are able to inhabit what on Earth are considered extreme or stressful environments. Cyanobacteria are observed to form crusts on dry, hot sand dunes in deserts (Karnieli *et al.*, 1999). They are also found in extreme cold in snow and ice (Mueller *et al.*, 2005), as are snow algae (Gorton *et al.*, 2001). Both desert crusts and marine water are highly saline environments, and marine microbial mats are inhabited by a range of anoxygenic photosynthesis bacteria and cyanobacteria (Decker *et al.*, 2005). A low pH extreme has been observed for the alga *Cyanidium caldarium* living at pH 0 (and at 56°C) (Schleper *et al.*, 1995), and a high pH of 10 for cyanobacteria (Finlay *et al.*, 1987). The anoxygenic photosynthetic bacteria (listed in Table 1), of course, survive in anoxic environments, as well as in conditions of low visible light (e.g., *B. viridis*). The light limits of photosynthesis are summarized in the next section.

3.5. Light quantity

Some organisms may function better in low or high light environments. The lower light limit is determined by the balance between photosynthesis and respiration, the cutoff between survival and death (the “light compensation point”), while the upper limit is determined by other resource limits (water, nutrients, carbon source) and the ability to protect against photooxidation (damage to Chl due to excited states of O_2 in high light). Rather than quantifying light in terms of energy, we express it here in photons (or moles of photons) because photosynthesis depends on

photon flux (at particular wavelengths) rather than energy flux. The lowest observed light compensation points are $\sim 3 \mu\text{mol}$ of photons $\text{m}^{-2} \text{s}^{-1}$ (0.7 W/m^2 , 1.8×10^{18} photons $\text{m}^{-2} \text{s}^{-1}$) of PAR for green plants (Nobel, 1999) and $\sim 0.01 \mu\text{mol}$ of photons $\text{m}^{-2} \text{s}^{-1}$ for red macro-algae [6×10^{15} photons $\text{m}^{-2} \text{s}^{-1}$ (Littler *et al.*, 1986)]. Overmann *et al.* (1992) observed a brown sulfur bacterium, living at ~ 80 m depth in the Black Sea, that is adapted to an available irradiance of $0.003\text{--}0.01 \mu\text{mol}$ of photons $\text{m}^{-2} \text{s}^{-1}$ ($1.8\text{--}6.0 \times 10^{15}$ photons $\text{m}^{-2} \text{s}^{-1}$) (additional characterization by Manske *et al.*, 2005). The theoretical unicellular light limit has been estimated by Raven (1984) to be $\sim 0.1 \mu\text{mol}$ of photons $\text{m}^{-2} \text{s}^{-1}$ (6×10^{16} photons $\text{m}^{-2} \text{s}^{-1}$), and as this is higher than that observed, additional efficiency strategies for survival at low light must be more a possibility than current understanding allows. Recently, Beatty *et al.* (2005) discovered a green sulfur bacterium that utilizes geothermal light at a hydrothermal vent, where the irradiance close to the vent is comparable to that at the 80 m depth of the Black Sea. This opens up the possibilities for photosynthesis independent of starlight. However, it is unlikely that these bacteria evolved under such low light conditions, but we think they probably are migrants from surface waters. For the upper limit of photon flux density, Wolstencroft and Raven (2002) summarized the literature and found a theoretical tolerance for land plants against photodamage at $6\text{--}9 \text{ mmol}$ of photons $\text{m}^{-2} \text{s}^{-1}$ ($3.6\text{--}5.4 \times 10^{21}$ photons $\text{m}^{-2} \text{s}^{-1}$) over the PAR band, which is well above Earth's typical flux of 2 mmol of photons $\text{m}^{-2} \text{s}^{-1}$ (1.2×10^{21} photons $\text{m}^{-2} \text{s}^{-1}$). For Earth-like planets in general, they conjectured a theoretical upper limit for land organisms to be 10 mmol of photons $\text{m}^{-2} \text{s}^{-1}$ (6×10^{21} photons $\text{m}^{-2} \text{s}^{-1}$). Since aquatic organisms are shielded under water, they could exist for even higher surface photon flux densities.

3.6. UV light damage

UV light is damaging to DNA, and exposure to UV at levels received at the Earth's surface generally inhibits photosynthesis and leaf expansion (Karentz *et al.*, 1994; Nobel, 1999; Tenini, 2004). Therefore, most of the discussion on UV effects on habitability focuses on protection against UV by ozone or microenvironments (Kasting, 1997; Cockell, 1999; Cockell and Raven, 2004), behaviors such as photomotility to avoid the harmful

UV (Bebout and Garcia-Pichel, 1995), and specialized screening pigments or phenolics that prevent the penetration of UV light into the cell [scytonemin in arctic cyanobacteria (Mueller *et al.*, 2005), phenolics in snow algae (Gorton and Vogelmann, 2003), and mycosporine-like amino acids in response to UVB photoreceptors in cyanobacteria and algae (Portwich and Garcia-Pichel, 2000; Hernando *et al.*, 2006)]. Such protective compounds may have played a role in the early emergence of plants onto land (Cooper-Driver, 2001) [scytonemin found in ancient rocks by Marilyn Fogel (personal communication), NASA Astrobiology Institute Conference, 2005]. The maximum flux of UV at the Earth's surface is $1.8\text{--}2.8 \times 10^{18}$ photons $\text{m}^{-2} \text{s}^{-1}$ over the UVB (280–315 nm) band at the Equator at noon under cloudless conditions, or averages globally $0\text{--}12 \text{ kJ m}^{-2} \text{ day}^{-1}$ (2.1×10^{17} photons $\text{m}^{-2} \text{s}^{-1}$, converting with the average energy per photon in the UVB). Damage to plants from UVB radiation has been observed at doses of $15\text{--}16 \text{ kJ m}^{-2} \text{ day}^{-1}$ [$2.6\text{--}2.8 \times 10^{17}$ photons $\text{m}^{-2} \text{s}^{-1}$ (Kakani *et al.*, 2003)].

3.7. Nutrients

Nutrients, as mentioned earlier, are also limiting resources. The nature of the limitation is on level of productivity and competitive advantage, rather than physiological tolerance. On land, the succession of species is often a function of the long-term development of the soil, which progresses through the release, addition, and eventual occlusion or loss of minerals and nitrogen. A comprehensive review of nutrient cycling is beyond the scope of this paper, but we summarize the most important limits here. Fixed N (available in the soil as NO_3^- and NH_4^+) and the minerals P, K, S, Mg, Fe, and Mn are the nutrients required for the production of pigments and enzymes, with N and P generally being the most limiting nutrients. Nitrogen is the main limiting nutrient, and its content in photosynthesizers is the prime correlating variable with photosynthetic capacity (Schulze *et al.*, 1994), since the Chls are tetrapyrroles with four nitrogen atoms surrounding a magnesium atom (Nobel, 1999), and the other pigments and proteins of the photosynthetic apparatus have even higher nitrogen content (Raven, 1984). Nitrogen must be fixed originally from atmospheric N_2 by enzymatic processes that occur in only particular organisms

and form NO_3^- and NH_4^+ . Availability is constrained, on land, by ecosystem age (time required for nitrogen fixing organisms to input nitrogen from the atmosphere into developing soil) and losses by leaching or fire. In aquatic and marine environments, availability is constrained by diffusion from the atmosphere and deposition from land-surface runoff of organic compounds. Mineral nutrient availability is locally constrained by rock substrate, geothermal sources, and deposition from non-local sources. Phosphorus, an essential mineral for DNA, ATP, and phospholipids of cell membranes, becomes available from weathering of the mineral apatite but then, over time, complexes with Al, Fe, and Mn (at low pH) or with Ca (at high pH), such that it becomes unavailable. In aquatic or ocean environments, Fe and P in addition to N are the primary limiting nutrients, and are input via atmospheric deposition or river runoff. For more details, the reader is referred to Schlesinger (1997).

4. SPECTRAL SIGNATURES OF PHOTOSYNTHETIC ORGANISMS

Given the above information on photosynthesizers' metabolism, pigments, and environmental niches, how do these features combine into the spectral reflectance of the whole organism? Figure 2c shows the surface incident photon fluxes of the Sun/Earth (in millimoles) with reflectance spectra of an oak leaf, a grass, a moss, and a lichen. On first glance, the red edge features appear to show some striking correlations with atmospheric absorbance features, particularly oxygen and water bands. We wish to find a physiological explanation. Physical explanations of land plant spectral signatures are fairly well understood in some aspects, whereas there is less of such information on other photosynthesizers. In this section, we first detail the reflectance properties of plant leaves. We then compare the reflectance spectra of other photosynthetic organisms to identify evolutionary pressures that would lead to variations, if any, particularly with regard to the "red edge."

4.1. Components of plant leaf spectral reflectance: physical explanation

Grant (1987) and Vogelmann (1993) reviewed in detail the optical properties of plant leaves, so only a brief summary from these reviews is pro-

vided here. In addition, the reader is referred to Tucker (1976, 1978) for discussion of satellite sensor bands for monitoring whole vegetation canopies.

Figure 2c shows the typical reflectance signature of land plants, for which the significant features include the green bump in reflectance and the "red edge." The latter is so-called because plant photosynthetic pigments absorb strongly in the visible or PAR, which strongly contrasts with high scattering in the NIR due to refraction between leaf mesophyll cell walls and air spaces inside the leaf. The wavelength of the "red edge" is more strictly defined as the inflection point in the slope of the reflectance between the red and NIR, and is sometimes referred to as the "red edge inflection point" or the "red edge position." It falls generally around 700 nm, but the location and steepness may vary according to the organism's abundance or thickness (if sensing over a large area) and physiological status; as shown later in this paper, there can be distinct differences between organism types.

Using the leaf radiative transfer model of Jacquemoud and Baret (1990), we illustrate in Fig. 3 how a leaf's spectral reflectance can vary according to (a) leaf structure and content of (b) water, (c) Chl a and b, and (c) carbon. The leaf structure is the main determinant of the high reflectance in the NIR in the overall signature, as leaf thickness and interstitial air spaces between mesophyll cells determine the surfaces off of which NIR is scattered. The cell membranes are composed of lipids and proteins, and the cell walls of cellulose and lignin. The refractive index in crop plants has been measured as 1.333–1.48, with averages around 1.43 (the refractive index of air is 1.0, of water is 1.333, and of soybean oil is 1.48) (Gausman, 1974) [wavelength-dependent refractive index (Jacquemoud and Baret, 1990)]. Note that, in fact, the cell walls also scatter visible light (Fig. 3c, gray line with no Chl a and b), but pigments absorb here when present. Water content affects reflectance in the longer wavelengths, with strong absorbance bands at ~1,400 nm and ~1,900 nm. In fact, the exact locations of these bands in the organism may shift with physiological status. Hydration status of a leaf positively affects the NIR reflectance, since cell turgor affects air spaces within the leaf. The Chl a and b content, of course, affects the absorbance in the visible. The carbon density affects just the reflectance bands in the NIR. The absolute

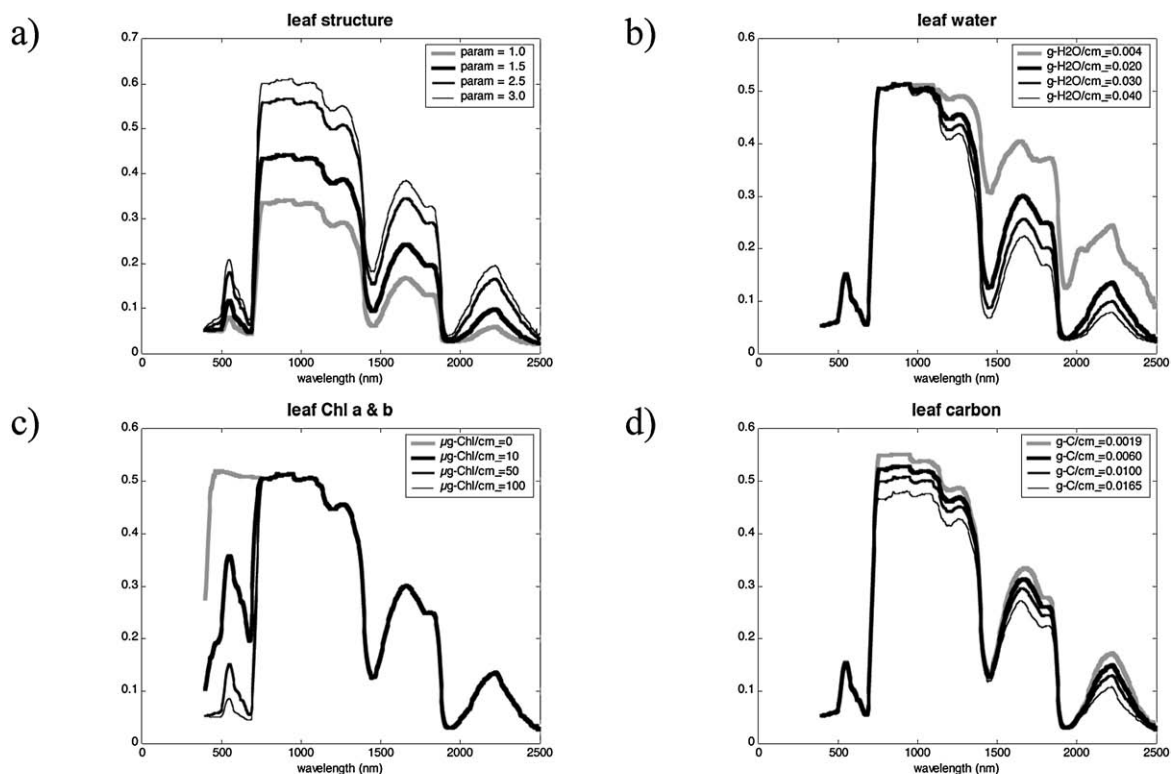


FIG. 3. Modeled reflectance spectra of a generalized plant leaf, from the model PROSPECT (Jacquemoud and Baret, 1990). Variations in reflectance are due to (a) structure, (b) water content, (c) Chl a and b content, and (d) carbon content.

red/NIR contrast, in general, increases for thicker leaves or multiple layers of leaves or organisms, as more Chl per area will absorb more in the visible, and more layers and interstitial air spaces increase the surfaces for NIR scattering per unit area. A weaker observed contrast with the NIR may be possibly due to properties of the organism surface, which we will detail later when comparing organisms.

The model of Jacquemoud and Baret (1990), based on a plate representation of the leaf (leaf structure is just a tunable parameter), represents well the vertical variations in the spectral reflectance in response to the given parameters. It does not deal with horizontal variations (wavelengths of critical features) such as variation in other pigments that affect the visible spectrum, observations that the NIR end of the red edge may broaden in curvature and shift in location, and observations that the water absorbance bands may blue- or red-shift with physiological status due to, for example, water stress or phenological changes (Filella and Penuelas, 1994; Penuelas and Filella, 1998; Karnieli *et al.*, 1999).

The nature of these shifts in the NIR reflectance has not been well studied.

4.2. Variations in reflectance spectra among photosynthetic organism types

Now, we offer perhaps the first attempt at a comprehensive comparison of reflectance spectra across photosynthetic taxa to determine whether this will yield further insights into how such spectra may have evolved. In particular, we focus on how the red edge varies among organisms, because this is the strongest feature that spectrally differentiates photosynthesizers from the background surface or water. The red edge begins at about 680 nm, where Chl a peaks in its absorbance in PS II (antenna of both PS II and PS I absorb almost equally 680 nm light), and then the reflectance plateaus around 720–760 nm. An evolutionary explanation for why these features occur at those particular wavelengths is not settled, particularly with regard to the NIR reflectance. Our driving questions here are where does the red edge begin, where does it end, and where

could it occur on another Earth-like planet, if at all?

Since the red edge is not merely a step function but has a slope with a bottom in the visible and a top in the NIR, various workers have tried to quantify the location of the red edge to distinguish species or quantify variations due to physiological status. The first derivative of the reflectance with respect to wavelength is a common measure by which to identify the point of maximum slope of the red edge, the “red edge inflection point.” Some workers take this point as the strict definition of the red edge, but here we will use “red edge” to encompass the span of the rise in reflectance from the visible to the NIR. The red edge inflection point varies with the level of the red absorbance and NIR reflectance, as well as with shifts in the wavelength of the onset of the NIR plateau. Therefore, we hypothesize that the wavelength of the NIR end may have more physical meaning than the red edge inflection point. For this wavelength of onset of the NIR plateau, we will coin the term the “NIR end.”

This NIR end is at least a function of the spectral spread of pigment absorbance, which, as we mentioned earlier, is affected by the proteins in which the pigments are bound. We are interested in surveying the variation in this NIR end and discerning whether it is the result of any environmental adaptations. Quantification of the location of this NIR end is not entirely straightforward because of the variations in curvature and slope that can occur over the NIR end and NIR plateau, respectively. We found the third derivative of the reflectance with respect to wavelength to capture fairly well the point at which the NIR plateau begins to level off, as this quantifies the “jerk” or change in the acceleration of the slope. The second derivative identifies better the point just before the NIR onset begins, rather than the plateau side. Because these measures are still somewhat subjective, we also calculate the first derivative as a well-defined measure of at least relative differences between spectra.

4.2.1. Presence of the red edge across photosynthetic taxa. Figure 4 shows spectral reflectance measurements (not a model) of (a) land-based vascular plants, (b) aquatic vascular plants, (c) mosses, (d) lichens, (e) algae, and (f) different layers of a microbial mat in an alpine lake (species and sources are summarized in Appendix A3). From this survey, it appears that all photosyn-

thesizers except the purple bacteria (Fig. 3d) have a “red edge,” albeit this edge is weak in lichens and bacteria. For organisms under water, the NIR plateau in the range 760–850 nm would be absorbed by water and not visible from above, but apparently, as seen from the aquatic plants’ spectra here, when removed from the water, the refractive properties with the air are such that these organisms also have a red edge.

In stark contrast, Fig. 4e shows that the purple bacteria clearly have no red edge, but instead show strong absorbance in the NIR and possibly adjacent NIR “edges.” The green sulfur bacteria exhibit red edge-like reflectance, with variation in the pigments in the visible. The orange line is of a mixture of filamentous bacteria, diatoms, and precipitations of elemental sulfur; a red edge feature also appears in this mix. All spectra in Fig. 4e are *in situ* measurements of whole mat layers (but outside the water) of species from the same microbial mat in an alpine bog pond (Wiggli *et al.*, 1999; data courtesy of Reinhard Bachofen). The purple bacteria are *Chromatium* species, anoxygenic photolithoautotrophs with BChl a or BChl b, and engage in sulfide reduction. The green sulfur bacteria are also anoxygenic and utilize BChl a, c, d, and e, with the latter three BChls having absorption peaks in the range 718–750 nm. The colonies may be mixed with oxygenic bacteria, such that the spectrum is not purely green sulfur bacteria. More measurements are needed to confirm distinct spectra for these different kinds of bacteria. Figure 4g shows reflectance spectra of various nonphotosynthetic surfaces, mineral and organic, including human skin and dead grass. Hematite and (live) human skin show some striking similarities to the photosynthetic organism spectra in that they have a color in the visible and high reflectance at longer wavelengths, but which are very different from those of the red edge features.

4.2.2. Horizontal variations in the NIR end across taxa. Figure 5 shows enlargements of the red edge section of the reflectances in Fig. 4, with the 761 nm oxygen absorption line as a reference that reveals differences in the wavelength of the NIR end. As an example of how we calculate the NIR end, Fig. 6 shows the third derivative of reflectance (left plot) and the reflectance spectrum of an aquatic plant. The vertical line indicates the maximum of the third derivative and the NIR end. Figure 7 shows a scatter plot of (a) the NIR end wavelengths of the spectra by organism type

and (b) the maximum slope wavelengths for the same spectra. There are clear trends by organism type: the terrestrial plant NIR end is reddest, ranging from 746 to 765 nm; aquatic plants cluster blue-ward of land plants at 730–745 nm; and mosses, temperate lichens, and temperate algae range from 720 to 733 nm. The snow algae have the bluest red edge. Because of the noisiness of the snow algae data, we could not calculate the NIR end, but the maximum slope wavelength shows clear trends. Also, because of interference of atmospheric oxygen, some reflectance spectra have a spike at 761 nm.

From this survey, it appears that the NIR reflectance, though common, does not appear to be universally the same among all photosynthetic organisms, but there appear to be consistent variations among taxa. Lichens often have no sharp edge, but a steady slope. Purple bacteria have possibly an NIR edge, which is consistent with their pigment absorbance spectra. There seems to be a trend in the “NIR end” (where the NIR reflectance begins to plateau in the red edge), in which the most structurally advanced to simplest organisms are ordered from reddest to bluest. More research is needed to explain these trends.

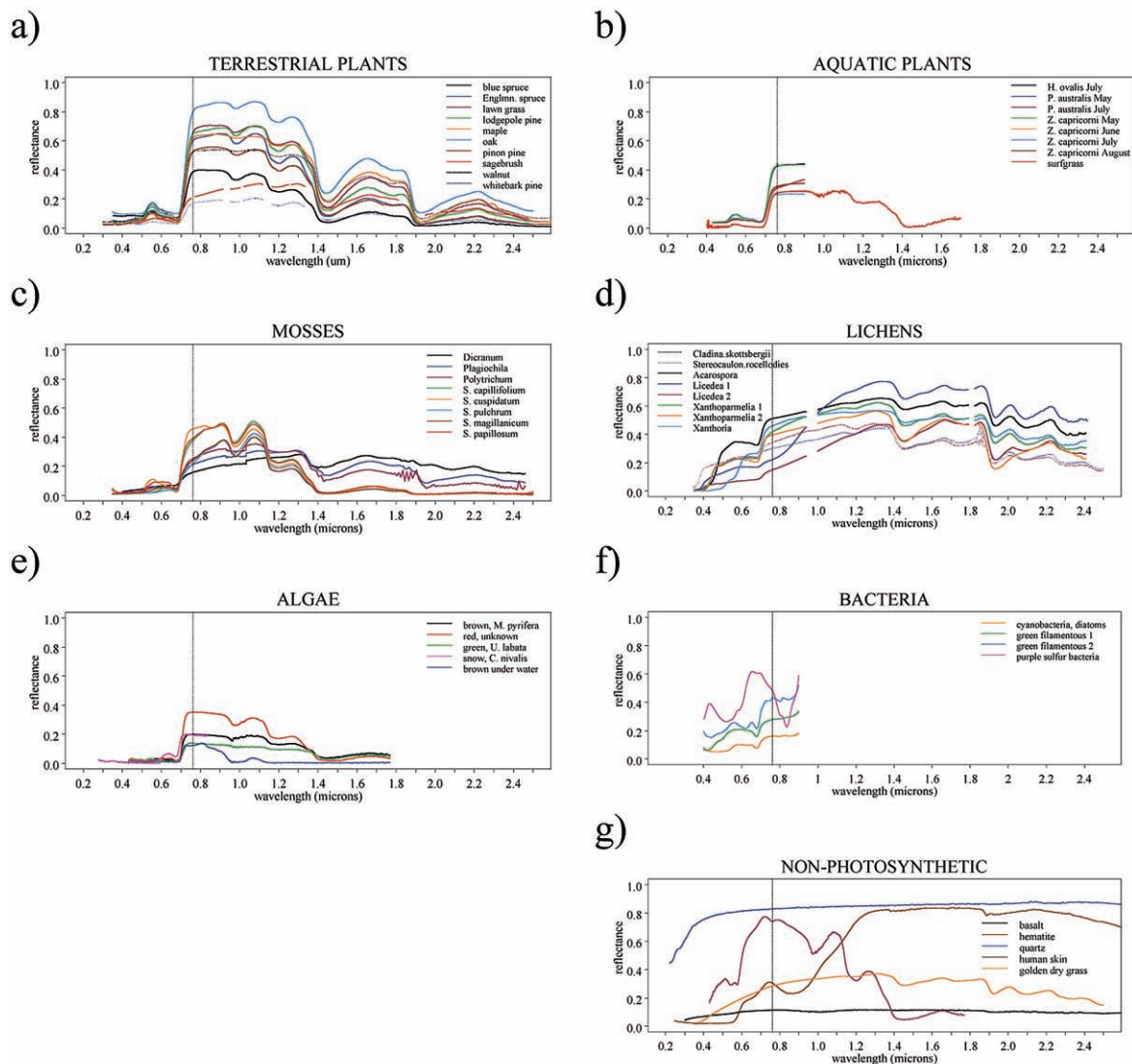


FIG. 4. Reflectance spectra of different photosynthetic organisms, minerals, and non-photosynthetic organic matter in the 0.2–2.4 μm range. The vertical dotted line in all the plots is at 0.761 μm , corresponding to an oxygen absorption line. Sources: (a) Land plants, Clark *et al.* (2003); surfgrass, aquatic plant, N.Y. Kiang. (b) Aquatic plants, Fyfe (2003); surfgrass, N.Y. Kiang. (c) Mosses, Lang *et al.* (2002), Harris *et al.* (2005). (d) Lichens, *Cladina* and *Stereocaulon*, courtesy of Greg Asner; *Acarospora*, *Licea*, *Xanthoparmelia*, and *Xanthoria*, Clark *et al.* (2003). (e) Algae, N.K. Kiang; snow algae, Gorton *et al.* (2001). (f) Bacteria in a microbial mat, from Reinhard Bachofen in Wiggli *et al.* (1999). (g) Minerals and golden dry grass, Clark *et al.* (2003); human skin, N.Y. Kiang. Species names and instruments used are listed in Appendix A3.

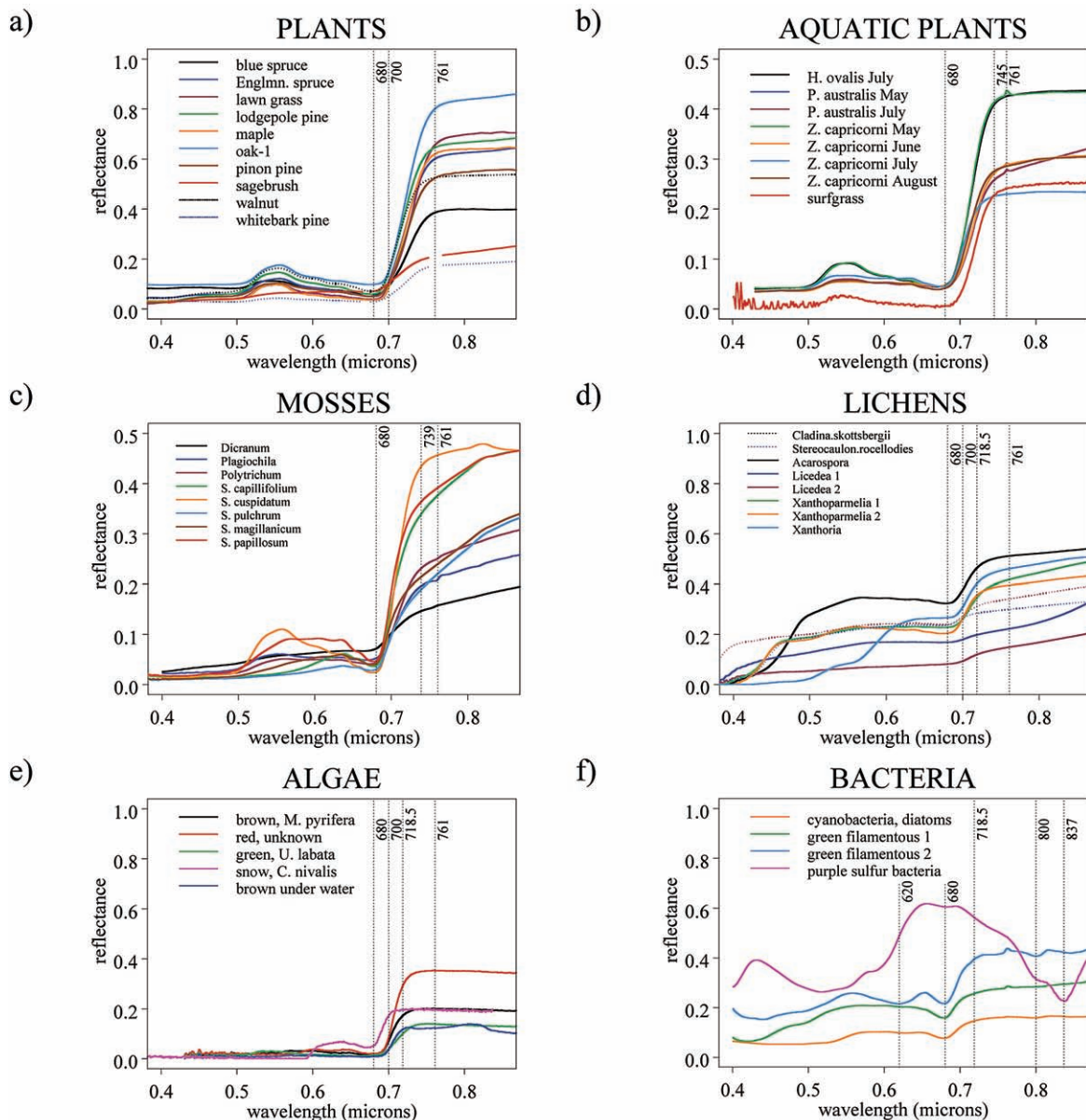


FIG. 5. Details of Fig. 4. Reflectance spectra of different photosynthetic organisms, minerals, and non-photosynthetic organic matter over 0.4–0.9 μm . Sources: Same as for Fig. 4. (a) Land plants, Clark *et al.* (2003); surfgrass, aquatic plant, N.Y. Kiang. (b) Aquatic plants, Fyfe (2003); surfgrass, N.Y. Kiang. (c) Mosses, Lang *et al.* (2002), Harris *et al.* (2005). (d) Lichens: Clark *et al.* (2003). (e) Algae, N.Y. Kiang; snow algae, Gorton *et al.* (2001). (f) Bacteria in a microbial mat: from Reinhard Bachofen in Wiggli *et al.* (1999).

5. EVOLUTIONARY RATIONALES FOR PHOTOSYNTHETIC SURFACE SPECTRAL REFLECTANCE

How the properties of pigments, cell membranes, and cell walls evolved is not well known, but some evolutionary rationale is needed, with regard to why particular spectral features of photosynthetic organisms occur at particular wavelengths, before we can conjecture where similar

features might arise on another planet. From what we have observed of Earth photosynthesizers, it seems especially important to know the evolutionary pressures on the following features: (1) photosynthetic RC excitation wavelengths, (2) core antenna peak absorbances, (3) accessory pigment peak absorbances, (4) beginning and ending wavelengths of the red edge, and (5) NIR reflectance bands. The primary evolutionary pressures or constraints may have been chemi-

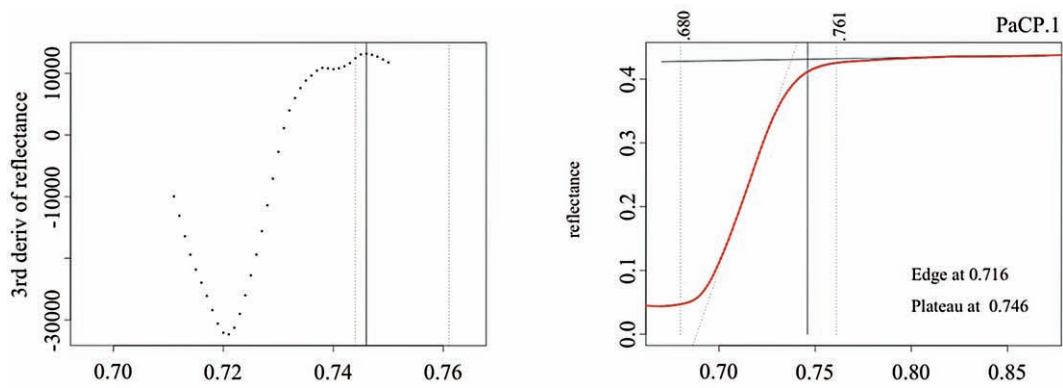


FIG. 6. Calculation of the NIR end wavelength for the aquatic plant *Posidiana australis*. The vertical solid thin line is the location of the third derivative maximum and the NIR end of the spectral reflectance (data courtesy of Susan Fyfe).

cal or thermodynamic, environmental, and ecological.

5.1. Pigment absorbance energetics

Here, we examine why the peaks in pigment absorbance are at their particular wavelengths, other than due to being in a light transmittance window.

5.1.1. Minimum energy requirements at the RCs: thermodynamics. Conversion of electronic photon energy to chemical energy occurs at the RCs. In brief, the energy requirements for this to happen are that the ground state of the primary donor Chl of an RC be at a higher redox potential than the reductant in order to oxidize it, and the photon must be of sufficient energy to excite the pri-

mary donor to a sufficiently low redox potential so that it can reduce various intermediates to reduce the final electron acceptor. So, the RC primary donor must straddle the roles of both oxidant in its ground state and reductant in its excited state (Blankenship and Hartman, 1998). In oxygenic photosynthesis (Eq. 2), the excitation, electron abstraction, and reductions are achieved in a two-step zig-zag series of potential changes (the “Z-scheme” mentioned earlier), where the reductant H₂O replaces the lost electron from the ground state of Chl a (P680 at 680 nm) in PS II, and PS II supplies the electron to replace that in PS I (P700 at 700 nm), which generates the reduced product eventually used for fixation of CO₂. P680 of PS II is at a higher potential than the water, allowing it to be a strong oxidant of water (Tommos and Babcock, 2000; Blankenship, 2002).

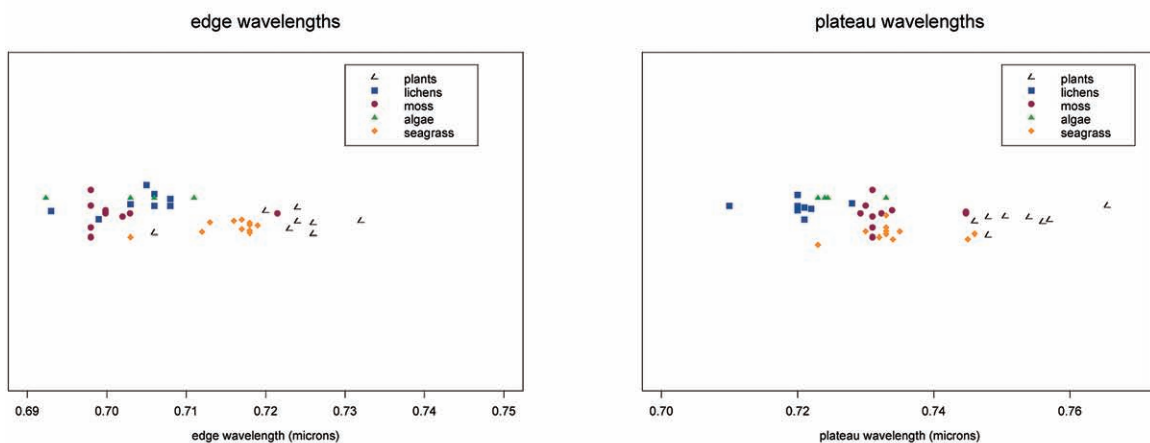


FIG. 7. Scatterplot of wavelengths of the red edge inflection point (“edge wavelengths”) and the NIR end (“plateau wavelengths”) for organisms in Figs. 4 and 5. The vertical axis has no scale, but points are dithered vertically simply to show their horizontal spread.

The potential difference of P680 from water results from the molecular configuration of the remarkable RC of PS II. Note that oxidation of water does not depend on the wavelengths of the photons used, but on the midpoint redox potential of the oxygen-evolving complex and the RC relative to water. In bacterial systems, the potential span afforded by RCs absorbing at 800, 850, and up to 960 nm is smaller and adequate for these other electron donor/acceptor combinations. But, thus, we are still left with the question, why—on Earth—is P680 at 680 nm, or, more generally, why are the other RCs at their exact wavelengths? If there is no thermodynamic necessity, then perhaps the driving force must be environmental pressure on what light can be harvested.

5.1.2. Excitation energy transfer between LHCs and RC: kinetics. In plants and most other photosynthetic organisms, the Chls have peak absorbances at the longest wavelength and, hence, lowest energy compared to the other pigments, which allows the energy cascade via resonance transfer to work. In PS II, the RC's (longest) peak absorption wavelength is at 680 nm (P680), and in PS I it is at 700 nm (P700). In anoxygenic bacteria, the known RCs are P800 (heliobacteria), P840 (green sulfur bacteria), P870 (purple bacteria, various sulfur and non-sulfur species), P870 (green filamentous, *Chloroflexus aurantiacus*), and P960 (*Blastochloris viridis*) (the actual peak is somewhat variable dependent on the core antenna environment) (Blankenship and Prince, 1985; Ke, 2001). The core antennae are generally integral to the RC complex, but may have slightly different spectral peaks. The Chls and BChls also harvest light at a major peak in the blue, but the RCs operate at the red peak. There are generally about 300 antenna Chls per RC Chl.

In green sulfur bacteria, green filamentous bacteria, heliobacteria, and cyanobacteria, the core antennae absorbance spectra peak at shorter wavelengths than the RCs, though there is considerable spectral overlap. In purple bacteria, the core antennae peak at longer wavelengths than the RCs [B1015 in *B. viridis* whose RC is P960, B890 in several purple bacteria that have P870, and B875 in *Rhodobacter sphaeroides*, whose RC is P870 (Ke, 2001; Blankenship, 2002; Scheer, 2003; Richard Cogdell and Andrew Gall, personal communication, data in Fig. 1b)]. So, interestingly, light absorbed at wavelengths longer than the

RCs can be transferred *up* the energy hill to the RCs (Trissl, 1993; Bernhard and Trissl, 2000; Permentier *et al.*, 2001). The transfer mechanism continues to be the subject of debate and research. In most purple bacteria, the spectral overlap of the RCs and core antennae is sufficient such that thermal variability is enough to prevent exciton energy from being trapped in the core antennae; however, the wavelength separation between the RC and core antenna peaks of *B. viridis* seems to require some other means of energy transfer. Trissl (1993) proposed a model of the transfer kinetics and trapping times; assuming a fast thermal equilibration of the excitation energy before the charge separation and constraints on quantum yield, the model seems to explain that the longer wavelength absorption does not affect the trapping time or the quantum yield, and it is profitable for the organism since this allows utilization of the available light. This seems to provide a sensible explanation for the uphill exciton transfer from BChl b at 1,013 nm to the RC at 980 nm. Mauzerall and co-workers (Boichenko *et al.*, 2001; Hou *et al.*, 2001a,b) quantified, in detail, the entropy changes that occur in PS I, PS II, and cyanobacteria, and found them to be very small. Work on kinetics of exciton transfer (Trissl, 1993; Trissl *et al.*, 1999; Bernhard and Trissl, 2000) implies the optimality of arrangements between the RCs and the light harvesting antennas to ensure efficient transport and trapping of the excitons.

The above theoretical work does not allow for prediction of the wavelength of the RCs, but it does offer an explanation of the excitation energy transfer kinetics between the RCs and the LHCs. The bulk of photosynthetic activity in *B. viridis* and other purple bacteria is probably driven by mostly shorter-wavelength photons (David Mauzerall, personal communication), but still, nature finds ways to harvest the available light. The light absorbed to 730 nm by oxygenic photosynthesizers also gets transferred uphill to the P700 RC, but this is just the tail end of the absorption spectrum of Chl in P700 and presumed not to contribute a large amount to the total photosynthetic activity. However, Krausz *et al.* (2005) found that there is charge separation in PS II in spinach even over the range 700–730 nm. So, uphill energy transfer is not the most productive way to obtain energy, but nonetheless the phenomenon indicates more means of light harvesting, while resonance transfer of energy toward the red is the dominant means of light harvesting and energy trapping.

In general, the literature on light harvesting has focused on excitation energy transfer kinetics, while the literature on RCs has focused on figuring out the molecular structure and mechanisms, genetic lineage, and molecular evolution (Xiong *et al.*, 2000; Dismukes *et al.*, 2001; Ferreira *et al.*, 2004; McEvoy *et al.*, 2005; Xiong, 2006). Meanwhile, theoretical work on the chemical evolution of Chl and the PS II oxygen-evolving complex is based on ancient ocean chemistry (Mauzerall, 1976; Blankenship *et al.*, 1998; Dismukes *et al.*, 2001; Dasgupta *et al.*, 2004) and provides energetic constraints on the steps toward the development of PS II. Little thus far has been done on solar radiation pressures on the evolution of pigment absorbance spectra, so we attempt to address such evolutionary drivers here.

5.1.3. Atmospheric spectral transmittance. The available light spectrum, of course, must be the first constraint on RC peak absorbance wavelengths. Numerous studies on diverse photosynthetic organisms have shown that the radiation absorption spectra of light harvesting pigments matches the spectrum of incident light in the organism's environmental niche. Examples include microbial mats at different water strata (Lengeler *et al.*, 1999; Eraso and Kaplan, 2001; Reinhard Bachofen, personal communication), purple and green photosynthetic bacteria in NIR and low light (Blankenship *et al.*, 1995), low-light plants (Marschall and Proctor, 2004), red algae and cyanobacteria absorbing in green wavelengths (Samsonoff and MacColl, 2001), and, recently discovered, cyanobacteria that perform oxygenic photosynthesis utilizing NIR radiation (Chen *et al.*, 2005).

In the wavelength locations of the onset and plateau of the red edge, several biological and atmospheric phenomena occur at both locations. Details of the charts in Fig. 3 are shown in Fig. 4 to illustrate more clearly the features around the red edge region. The bottom of the red edge varies little from 680 nm, which is the peak absorbance wavelength of most of the antenna Chls, as well as the primary donor PS II in plants, algae, and cyanobacteria. However, depending on measurement precision or perhaps cell structures, the onset can be as low as 670 nm (lichen, Licedea-1 in Fig. 4c) and does not appear to go beyond 700 nm, where some of the long-wavelength forms of antenna Chls absorb. Also, Chl, a primary donor of PS I, has its peak absorbance at

700 nm. Significant phenomena occur in the red edge region [Krausz *et al.* (2005) called it "spectral congestion" with regard to an even more detailed structural breakdown than summarized here] at the following wavelengths: 650–670 nm, where core antenna minor sub-bands occur for PS I and PS II; 678.5 nm, the main sub-band for PS II; 680 nm, the location of the primary donor P680 for PS II; 682 nm, the main sub-band for PS I; and 700 nm, the primary donor P700 for PS I. The main sub-bands are actually where most of the light harvesting of the core antenna occurs. From these data, it appears that the maximum absorbance at the foot of the red edge rarely departs from the 678.5 nm sub-band in organisms that utilize PS II.

Perhaps the most significant spectral feature to observe is that the maximum photon flux density at the Earth's surface occurs at 685 nm, just before a drop in atmospheric transmittance due to oxygen at 687.5 nm. The O₃ Chappuis band (500–700 nm) shifts the Sun's photon spectral flux density from its top-of-the-atmosphere peak at 600 nm to 685 nm at the Earth's surface, which may partially explain why Chl favors the red rather than the green. (Note that, at the Earth's surface, the incident energy flux peak is spread over 450–490 nm, in the green.) Thus, it appears that the peak absorbance at the foot of the red edge is an adaptation to harvesting light in the atmospheric transmittance window with the most abundant photon flux, and the peak is at the most red-shifted limit of that window to afford exciton transfer from accessory pigments at the shorter wavelengths in that window. The long wavelength limit of this window is due to both the solar spectrum and the presence of oxygen, the very product of photosynthesis. Note that, if the surface incident light spectrum is viewed in terms of energy flux rather than photon flux, the peak flux is around 480–490 nm, which is in the blue-green; since photosynthesis counts photons, not total energy, it is the peak photon flux that is favored by pigments. On the other hand, of course, if photosynthesis evolved originally under water prior to atmospheric oxygen buildup, then there is no good reason for the oxygen band to have supplied any evolutionary pressure on the RC peaks, unless such selective pressure continued to occur on near-surface organisms. However, this may explain why PS I and PS II of green cyanobacteria and green algae had the advantage in giving rise to land plants.

The NIR end of the red edge is clearly confined to wavelengths between the oxygen A-band at 761 nm and the bluest side of the water band at about 718 nm. Only the snow algae have an NIR end blue-shifted from this 718 nm. One might expect organisms under ice or water to have spectral characteristics adapted to these media in contrast to air. However, there is no distinctive feature for ice absorption or reflectance blue-ward of the water band, and for organisms under water, there is not clearly a tight relation with the water absorption band in our data. Figure 6b shows our one anoxygenic example together with the irradiance through water. It may be that the peak absorption wavelength of this purple bacterium is related to the water band at ~810–840 nm. More whole-organism reflectance data are needed to draw any firm conclusions, but, tentatively, we hypothesize that the NIR end has evolved in response to major absorbance bands of the air or water medium of the photosynthesizer.

Purple bacteria have a starkly different reflectance spectrum, with our one example showing an “NIR edge” (perhaps better called an “NIR slope”) rather than a red edge, starting at 837 nm. The BCHls for the purple bacteria and green non-sulfur bacteria result in primary donor or RC wavelengths at 840–960 nm. Unfortunately, few single-colony or whole-organism reflectance spectra have been measured of anoxygenic bacteria. The data here were measured only over 400–900 nm, so we cannot examine other NIR features or the spectrum of species like *B. viridis* that harvest light at longer wavelengths.

5.2. NIR scattering

As seen in Figs. 4–7, not all photosynthetic organisms exhibit the same degree of NIR scattering. Why does the NIR reflectance vary, whether due to environmental adaptations, physiological status, or other unexplained evidence?

5.2.1. Morphological adaptations to light and climate. It is well known that morphological adaptation to different climate limits and light levels will influence spectral characteristics due to differences in leaf thickness or canopy density. These quantities affect the boundary layer conductance at the leaf surface and light penetration into the leaf (where the leaf boundary layer is the gas diffusive layer of air at the surface). Thus, cold, dry environments favor needleleaf plants, wet,

temperate environments favor broadleaf species, and hot, dry environments favor succulents with low surface-to-volume ratios (Holdridge, 1967; Schuepp, 1993; Larcher, 1995; Foley *et al.*, 1996). Highly sunlit leaves are thicker, allowing for a greater absorption cross-section of PAR (Fitter and Hay, 1987; Kull, 2002); therefore, the visible/NIR contrast will be stronger for high light-adapted leaves. In addition, leaf surface characteristics, such as hairs or trichomes, specularity of the surface, and surface waxes, can affect the overall reflectance; hairs help increase albedo in hotter, brighter environments, while waxes may serve to absorb high UV in arctic environments.

5.2.2. Compactness of cells. A lower NIR reflectance may result from a lack of air spaces around more compact cells. For example, loss of cell turgor during water stress could reduce air–cell wall interfaces for NIR scattering. Lichens have a dense structure in a fungal cortex that overlies their cyanobacterial or algal layer, and, therefore, they are not highly reflective in the NIR. Conifer species have a dense mesophyll structure, and, hence, their leaves tend to be darker in the NIR than those of broadleaf plants. In contrast, *Sphagnum* mosses increase rather than decrease NIR reflectance when dried (dried spectra not shown), because their means of water supply to the plant’s capitula is not through internal conducting cells but through precipitation or capillary rise only (Harris *et al.*, 2005). Abundant hyaline cells provide a large water holding capacity in *Sphagnum*, but their drying results in structural changes much different from that of vascular plant leaf mesophyll cells. *Sphagnum magellanicum* (Fig. 4c, moss) has a very low-sloping red edge compared to the other mosses, due to more tightly bunched capitula.

5.2.3. Energy balance. Although the NIR reflectance must play some role in an organism’s energy balance, it is not clear how important this is in the organism’s survival and evolution of its spectral signature. In snow algae, Gorton *et al.* (2001) found a substantial NIR absorbance of the outer membrane, which could possibly afford a more favorable energy balance for the algae. On the other hand, as noted above, the NIR reflectance decreases in desiccated plant leaves but increases in dried mosses. Lichens, in both cold arctic and hot tropical environments, exhibit very low scattering (reflectance as well as transmit-

tance) in the NIR [transmittance <15% (Bechtel *et al.*, 2002)]. Aquatic plants and algae and cyanobacteria that grow under water have no clear need for an NIR reflectance to control their energy balance. The NIR reflectance can be found to vary by the same degree in diverse ecosystems across different environmental gradients, such that it is not straightforward to draw a conclusion about the NIR reflectance's role in an organism's survival or competitive advantage. Undoubtedly, it is important to some organisms, but there are not yet enough data to determine consistent trends. More studies are needed of the relation between the energy balance of photosynthetic organisms, their climatic limits, and their spectral reflectance signatures.

5.2.4. Cell wall refractive index and light transmission. The cell wall composition of organisms, of course, must have a definite functional role in exchange of gas and fluid, structural support (or not), and transmission of light, and it determines the spectral refractive index, as mentioned earlier. In Table 1, it can be seen that there are some differences between taxa. Terrestrial plant cell walls contain cellulose, lignin, polysaccharides, and protein, whereas aquatic plants contain little or no lignin, since it is not necessary for support. Algal cell walls are predominantly cellulose; dinoflagellates, which are the photosynthetic symbionts in corals and are responsible for algal blooms known as red tides, also have a theca, an armor-like set of plates beneath the plasma membrane (Evitt, 1985; Larkum and Veski, 2003). Cyanobacteria cell walls contain murein. Unfortunately, Table 1 is incomplete, since there are few data on cell wall compositions for other photosynthetic organisms. The cell wall composition of purple bacteria might not have very different refractive properties from that of other photosynthesizers, so long as the NIR radiation can be transmitted into the cell.

6. CONCLUSIONS

To summarize, the full reflectance spectrum of a photosynthetic organism is the expression of both molecular and macrostructural properties: (1) the absorbance spectra of the LHC, the core antenna complex, and the RCs; (2) cell membrane and cell wall refractive properties; and (3) whole-organism structural impacts on light scattering.

How the above properties evolved is not well known, but a number of environmental pressures and molecular constraints play a role: (1) the thermodynamics of light harvesting and exciton transfer kinetics; (2) the redox potential requirements for oxidation of the electron donor and reduction of CO₂; (3) adaptation to available resources (light spectrum, nutrients, electron donor), which is not covered in detail here; and (4) adaptation for protection against environmental harm (UV radiation, temperature, chemical toxicity, *e.g.*, levels of pH, O₂, other).

Electron abstraction from the reductant, such as H₂O, H₂S, or FeOH⁺, does not depend on the wavelength of the photon but on the redox potential of the biochemical molecule. The excitation of the RC Chl to a sufficiently energetic state does depend on the photon energy, and multiphoton pathways could theoretically utilize more photons at longer wavelengths to evolve O₂ and fix carbon. A long wavelength limit might be 1,100 nm, a threshold between optical and thermal or vibrational. The ability to perform electronic transitions, however, depends on the molecule, and more research is needed to define strict thermodynamic constraints. The kinetics of exciton transfer require sufficient proximity between light harvesting pigments and the RC for efficient trapping of the excitons, such that it is more energetically favorable for the RC to absorb at longer wavelengths; however, uphill electron transfer does occur. The spectrum of available light ultimately limits pigment absorption spectra and productivity.

For the full reflectance spectrum of the organism, we observed, on Earth, that the "red edge" is nearly ubiquitous among oxygenic photosynthesizers, but it is weak or negligible in lichens. For cyanobacteria, more data are needed. Although it is fairly well understood how the NIR reflectance varies due to morphology, the selective role of the NIR reflectance is not well understood. Thus far there is anecdotal evidence with regard to the organism's energy balance [and one study on crop leaves by Aboukhaled (1966)] and not enough data on the diversity of cell membrane and cell wall compositions. For anoxygenic photosynthetic bacteria that have their RCs in the NIR, the one example for purple bacteria shows no red edge, as it would not make sense for the organism to scatter light in the wavelengths that it utilizes. The green sulfur bacteria, oddly, appear to exhibit a bit of red

edge, so more measurements are needed to confirm whether this is the general case. The spectra we assembled show striking trends in the NIR end among organisms, with lichens, algae, and mosses most blue-shifted, terrestrial plants most red-shifted, and aquatic plants in the middle. More data on bacteria and algae across environmental gradients, along with consistent measurement of ambient conditions and assessment of the organism's physiological status, are needed to confirm the strength of these trends.

The Sun's radiation spectrum and the spectral transmittance of the atmosphere and water environments are the most important selective pressures on critical points in the pigment spectra of photosynthetic organisms. Atmospheric oxygen may have altered the atmospheric transmittance spectrum enough to favor PS I and PS II absorbance in the red. Meanwhile, the example of lichens indicates that not all photosynthesizers will necessarily have a steeply contrasting reflectance where pigments do not absorb and high NIR reflectance is not clearly an energy balance adaptation. So, we cannot conclude yet how a whole organism's reflectance spectrum, besides the pigment spectra, is a function of environmental adaptation. We do not have enough data on bacteria to draw conclusions about their reflectance properties, but the one purple bacteria example indicates that shifted spectral signatures are possible for organisms using anoxygenic photosystems. Resonance transfer and exciton transfer kinetics appear to work in concert with the available light spectrum to constrain the peak absorbance wavelength of the core antenna and RCs. Given the ability of organisms to transfer light energy both downhill and uphill to the RCs, it may be sufficient just to search for a pigment signature within particular atmospheric transmittance windows.

We can, therefore, propose the following candidates for photosynthetic pigment peak absorbance wavelengths:

1. The wavelength of peak incident photon flux within a radiation transmittance window, as the main environmental pressure.
2. The longest wavelength within a radiation window for core antenna or RC pigments, due to the resonance transfer of excitation energy and an energy funneling effect from shorter to longer wavelengths.

3. the shortest wavelengths within an atmospheric window for accessory pigments, also due to resonance transfer.

These hypotheses assume some optimality principle, where the peak photon flux wavelength is energetically and ecologically most favorable for survival, and organisms will have adapted to this. It may be that accidents, inertia, or the slow stages of evolution will not yield the optimum spectral signature for photosynthesizers at the time we observe them. For example, on Earth, the inefficiency of Rubisco (the carbon-fixing enzyme on which all photosynthesis depends and which sometimes is rendered useless for carbon fixation, because it also functions as an oxygenase) is the subject of much lament and agricultural biotechnological research (Parry *et al.*, 2003). Plant reflectance of green light is often considered a similarly suboptimal feature of plants, as there appears a spectral mismatch between solar radiation at the Earth's surface and the absorption peaks (440 and 680 nm) of Chl (Raven and Wolstencroft, 2002). Even with our rules above for pigment properties, there appears to be wasted green light. However, given that algae and cyanobacteria utilize phycobilins to harvest green light, the low harvesting of green light in land plants has been thought by some to be an inefficiency due to an evolutionary "lock-in" from the lineage of green algae. However, above-ground plant pigments do absorb green light, just in a lesser ratio to other colors, and they often experience too much light (or are limited by other resources), hence the need for quenching by carotenoids. The non-light harvesting pigment anthocyanin, which accumulates at the surface of shade-adapted leaves and makes them red, may provide photoprotection under high light by shading Chl b in chloroplasts from green light (Gould *et al.*, 2002; Pietrini *et al.*, 2002). So, there may be no selective advantage to absorbing more green light. That all land plants are descended from the green algae may very much be because their pigment combinations provided the selective advantage for life on land after the buildup of atmospheric O₂, which shifted the surface spectral photon flux from a peak at 600 nm to 685 nm. So, given some caveats about evolutionary optimality with regard to light resource constraints, we propose the above rules for wavelengths of peak photosynthetic pigment radiation absorbance, dependent on the spectral photon flux density at the surface of a planet.

7. APPENDIX A1: PHOTOSYNTHETIC PIGMENT ABSORBANCE SPECTRA

TABLE A1. PHOTOSYNTHETIC PIGMENT ABSORBANCE SPECTRA

Pigment	Object measured	Source
Chl a	<i>In vitro</i> spectra were stretched/shifted in wavelengths to match <i>in vivo</i> peaks by linear transformation	<i>In vitro</i> spectra from Junzhong Li (Du <i>et al.</i> , 1998)
Chl b	<i>In vitro</i> spectra were stretched/shifted in wavelengths to match <i>in vivo</i> peaks by linear transformation	<i>In vitro</i> spectra from Junzhong Li (Du <i>et al.</i> , 1998)
BChl a	Intact membranes in <i>R. sphaeroides</i>	Richard Cogdell and Andrew Gall (personal communication)
BChl b	Intact membranes in <i>B. viridis</i>	Richard Cogdell and Andrew Gall (personal communication)
BChl c	Green sulfur bacteria	Frigaard <i>et al.</i> (2004)
BChl d	Green sulfur bacteria	Frigaard <i>et al.</i> (2004)
BChl e	Green sulfur bacteria	Frigaard <i>et al.</i> (2004)
Phycocerythrin	Unpublished absorption spectra from Govindjee's laboratory [Beckman (Fullerton, CA) DU spectrophotometer]	Ke (2001), Govindjee (unpublished data)
Phycocyanin	Unpublished absorption spectra from Govindjee's laboratory [Beckman (Fullerton, CA) DU spectrophotometer]	Ke (2001), Govindjee (unpublished data)
Carotenoid	Estimated <i>in vivo</i> absorption spectra in green algae (note the type of carotenoid not specified)	Govindjee (1960)
Chl a fluorescence	Spinach chloroplasts	Govindjee and Yang (1966)

To explain whole-organism spectral reflectance and the steepness of absorbance peaks, more studies are needed of bacteria spectral properties, the role of pigment-protein complexes in altering pigment absorbance spectra, thermodynamic limits of light harvesting and redox biochemistry, field studies and modeling of organism radiative transfer, growth, and energy balances within their respective light environments, and further speculation on the environment of the early Earth.

8. APPENDIX A2: SPECTRAL TRANSMITTANCE OF LIGHT THROUGH ALGAE IN WATER IN FIG. 2B

In Fig. 2b, the light incident at a depth of 5 cm in water with algae was calculated by estimating an absorbance coefficient from a measured reflectance spectrum, scaling this absorbance coefficient to approximate a density of algae, and then calculating the light transmitted through, given the surface incident radiation in Fig. 2b. The attenuated light, $I(z, \lambda)$, at a depth of z cm at wavelength λ , given incident light at the surface of

$I(0, \lambda)$, spectral absorption coefficient of water $\alpha_{\text{water}}(\lambda)$ and of algae $\alpha_{\text{algae}}(\lambda)$, and a density parameter ρ_{algae} , is:

$$I(z, \lambda) = I(0, \lambda)e^{-(\alpha_{\text{water}} + \rho_{\text{algae}}\alpha_{\text{algae}})z} \quad (6)$$

For $\alpha_{\text{water}}(\lambda)$, we used water spectral absorption coefficient values as measured by the following sources: 200–380 nm, Segelstein (1981); 380–640 nm, Sogandares and Fry (1997); and 640–2,500 nm, Kou *et al.* (1993).

For $\alpha_{\text{algae}}(\lambda)$, we took spectral reflectance measurements of fresh samples of a brown alga, *Macrocystis pyrifera* (kelp), with a FieldSpec[®] Pro spectroradiometer (Analytical Spectral Devices, Inc., Boulder, CO) (borrowed from Mike Eastwood and co-workers at the Jet Propulsion Laboratory Airborne Visible/Infrared Imaging Spectrometer lab). Since we could not measure transmittance directly, we estimated transmittance from comparison to the behavior of a cloverleaf modeled by the PROSPECT leaf radiative transfer model of Jacquemoud and Baret (1990). A leaf transmittance spectrum is almost exactly the same as the reflectance, with the sum of reflectance and transmittance scattering

9. APPENDIX A3: PHOTOSYNTHETIC ORGANISMS' REFLECTANCE DATA

TABLE A3. PHOTOSYNTHETIC ORGANISMS' REFLECTANCE DATA

Organism type	Species measured	Instrument	Resolution	Source
Terrestrial vascular plants, temperate	Engelmann spruce, lawn grass, lodgepole pine maple oak piñon pine walnut	ASD FieldSpec	3 nm: 0.35–1 μm 10 nm: 1–2.5 μm	Clark <i>et al.</i> (2003) (USGS splib05a spectral database)
Aquatic vascular plants				
California coast	<i>Phyllospadix torreyi</i>	ASD FieldSpec 350–2500P	3 nm: 0.35–1 μm 10 nm: 1–2.5 μm	Nancy Kiang
Seagrass	<i>Zostera capricorni</i> <i>Posidonia australis</i> <i>Halophila ovalis</i>	ASD FieldSpec FR	3 nm: 0.35–1 μm 10 nm: 1–2.5 μm	Fyfe (2003)
Lichens				
Temperate	<i>Acarospora</i> <i>Licedea</i> <i>Xanthoparmelia</i> <i>Xanthoria</i>	ASD FieldSpec	3 nm: 0.35–1 μm 10 nm: 1–2.5 μm	Clark <i>et al.</i> (2003) (USGS splib05a spectral database)
Tropical	<i>Cladina skottsbergii</i> <i>Stereocaulon rocellodites</i>	ASD FieldSpec	3 nm: 0.35–1 μm 10 nm: 1–2.5 μm	Courtesy of Greg Asner
Moss (temperate)	<i>Dicranum</i> <i>Plagiochila</i> <i>Polytrichum</i> <i>Sphagnum capifolium</i> <i>Sphagnum cuspidatum</i> <i>Sphagnum pulchrum</i> <i>S. magellanicum</i> <i>Sphagnum papillosum</i>	ASD FieldSpec ASD FieldSpec Pro	3 nm: 0.35–1 μm 10 nm: 1–2.5 μm 1 nm: 0.35–2.5 μm	Clark <i>et al.</i> (2003) (USGS splib05a spectral database) Harris <i>et al.</i> (2005)
Algae				
California	Brown (<i>M. pyrifera</i>) Red (unknown) Green (<i>Ulva lobata</i>)	ASD FieldSpec 350–2500P	3 nm: 0.35–1 μm 10 nm: 1–2.5 μm	Nancy Kiang
Snow	<i>Chlamydomonas nivalis</i> (Bauer) Wille	Ocean Optics S-2000, #754	0.66 nm: 0.28–0.86 μm	Gorton <i>et al.</i> (2001)
Bacteria	Green filamentous Purple sulfur	ASD LabSpec VNIR-512 with optical fiber (LDG-GC 600/750, 25 m, Fujikuro, Tokyo, Japan)	1.5 nm	Reinhard Bachofen (personal communication), Wiggli <i>et al.</i> (1999)
Bacteria	<i>R. sphaeroides</i> <i>B. viridis</i>		0.5 nm	Richard Cogdell and Andrew Gall (personal communication)

ASD, Analytical Spectral Devices, Inc.; USGS, United State Geological Survey.

nearly all NIR near the red edge. Therefore, we estimated the kelp transmittance from a scaling of the reflectance to allow for about 5% absorbed NIR at the red edge, and then calculated the spectral absorbance as $1 - (\text{reflectance} + \text{transmittance})$. To approximate the density of the algae in water, we simply let $\rho_{\text{algae}} = 0.10$.

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11. ABBREVIATIONS

Bchl, bacteriochlorophyll; Chl, chlorophyll; LHC, light harvesting complex; NIR, near-infrared; PAR, photosynthetically active radiation; PS I, Photosystem I; PS II, Photosystem II; RC, reaction center; UV, ultraviolet.

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