Research Paper

Vegetation's Red Edge: A Possible Spectroscopic Biosignature of Extraterrestrial Plants

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ABSTRACT

Earth's deciduous plants have a sharp order-of-magnitude increase in leaf reflectance between approximately 700 and 750 nm wavelength. This strong reflectance of Earth's vegetation suggests that surface biosignatures with sharp spectral features might be detectable in the spectrum of scattered light from a spatially unresolved extrasolar terrestrial planet. We assess the potential of Earth's step-function-like spectroscopic feature, referred to as the "red edge," as a tool for astrobiology. We review the basic characteristics and physical origin of the red edge and summarize its use in astronomy: early spectroscopic efforts to search for vegetation on Mars and recent reports of detection of the red edge in the spectrum of Earthshine (i.e., the spatially integrated scattered light spectrum of Earth). We present Earthshine observations from Apache Point Observatory (New Mexico) to emphasize that time variability is key to detecting weak surface biosignatures such as the vegetation red edge. We briefly discuss the evolutionary advantages of vegetation's red edge reflectance, and speculate that while extraterrestrial "light-harvesting organisms" have no compelling reason to display the exact same red edge feature as terrestrial vegetation, they might have similar spectroscopic features at different wavelengths than terrestrial vegetation. This implies that future terrestrial-planetcharacterizing space missions should obtain data that allow time-varying, sharp spectral features at unknown wavelengths to be identified. We caution that some mineral reflectance edges are similar in slope and strength to vegetation's red edge (albeit at different wavelengths); if an extrasolar planet reflectance edge is detected care must be taken with its interpretation. Key Words: Red edge—Vegetation—Extrasolar planets—Light reflectance— **Spectroscopic biosignatures.** Astrobiology 5, 372–390.

INTRODUCTION

THE SEARCH FOR EXTRASOLAR terrestrial planets is in large part motivated by the hope of finding signs of life or habitability via spectroscopic

biosignatures. Spectroscopic biosignatures are spectral features that are either indicative of a planetary environment that is hospitable to life (such as the presence of liquid water) or of strong indicators of life itself (such as abundant O_2 in

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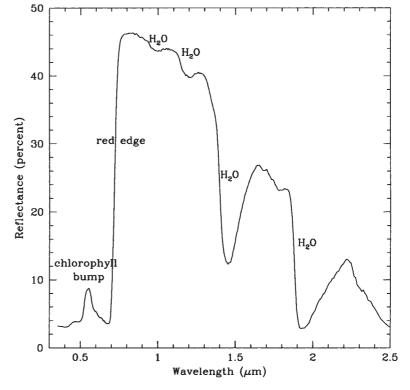
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the presence of CH₄). Most attention so far has been given to atmospheric biosignatures, gases such as O₂, O₃, H₂O, and CH₄ (Des Marais *et al.*, 2002). Instead we focus on a potential *surface biosignature*. An ideal surface biosignature would be produced by a large and abrupt change in the reflectance at wavelengths that penetrate to the planetary surface. Earth has one such surface biosignature: the vegetation red edge spectroscopic feature (Fig. 1).

Over 100 extrasolar giant planets are currently known to orbit nearby Sun-like stars (see http://exoplanets.org/, http://obswww.unige.ch/ ~udry/planet/coralie.html, and http://cfa-www. harvard.edu/planets/) (e.g., Butler et al., 2003; Mayor et al., 2003). These planets have been detected by the radial velocity method, which measures the star's line-of-sight motion due to its orbit about the planet–star common center of mass. Therefore, with the exception of a half-dozen known transiting planets, only the minimum mass and orbital parameters are known. Many efforts are underway to learn more about extrasolar planets' physical properties from groundbased and space-based observations and via proposed or planned space missions. Direct detection of scattered or thermally emitted light from the planet itself is the only way to learn about many of the planet's physical characteristics. Direct detection of Earth-size planets, however, is extremely difficult because of the extreme proximity in the sky of the parent star that is typically 10^6 – 10^{10} times brighter than the planet.

The Terrestrial Planet Finder (TPF) (see http://planetquest.jpl.nasa.gov/TPF/tpf/index. html) is being planned by NASA to find and characterize terrestrial planets in the habitable zones of nearby stars. [The habitable zone is defined as the annulus around the star where the planet equilibrium temperature range is consistent with surface liquid water (Kasting et al., 1993).] NASA is currently planning both a visible-to-near-infrared (IR)-wavelength mission (launch date 2014; wavelength range 500–1,050 nm) and a mid-IR-wavelength mission (launch date 2019; wavelength range 6.5–17 μ m) for TPF. The European Space Agency's Darwin mission (see http://sci.esa.int/home/Darwin/index.cfm) at mid-IR wavelengths has similar science goals. The primary focus of these space missions is the direct detection of extrasolar terrestrial planets and the spectroscopic characterization of their atmospheres. In addition to the previously mentioned atmospheric biosignatures, O₂, O₃, H₂O,

FIG. 1. Reflection spectrum of a deciduous leaf (data from Clark *et al.*, 1993). The small bump near 500 nm is a result of chlorophyll absorption (at 450 nm and 680 nm) and gives plants their green color. The much larger sharp rise (between 700 and 800 nm) is known as the red edge and is due to the contrast between the strong absorption of chlorophyll and the otherwise reflective leaf.



and CH₄, other atmospheric features such as CO₂ and Rayleigh scattering as well as physical characteristics such as temperature and planetary radius could be constrained from low-resolution spectra (see, *e.g.*, Seager, 2003). Beyond TPF, NASA is contemplating a series of increasingly ambitious astrobiology missions with evocative names such as Life Finder and Planet Imager.

New ideas are being developed to maximize science return from TPF. We have shown (Ford et al., 2001) that several important planetary characteristics could also be derived from photometric measurements of the planet's time domain variability at wavelengths from 400–800 nm. A time series of photometric data of a spatially unresolved Earth-like planet could reveal a wealth of information such as the existence of weather, the planet's rotation rate, the presence of large oceans or surface ice, and the existence of seasons. This would be possible for other planets if the observed light is scattered by at least two different scatterers that have significant differences in their albedo, color, or directionality of scattering. The amplitude variation of the time series depends on cloud-cover fraction; more cloud cover raises the average albedo of the planet and makes it more photometrically uniform, thus reducing the fractional variability. The signal-to-noise ratio necessary for photometric study would be obtained by any mission capable of measuring the sought-after atmospheric biosignature spectral features. Furthermore, the photometric variability could be monitored concurrently with a spectroscopic investigation, as was done for the transiting extrasolar giant planet HD209458b (Charbonneau et al., 2002).

Serious attention to the possibility of spectroscopic detection of surface biosignatures on extrasolar plants is relatively recent, even though interest in spectroscopic signatures of vegetation on planets in the Solar System has a long history (see Red Edge Observations Within the Solar System). The pioneering detection of Earth's vegetation red edge feature in the spectrum of Earthshine by Woolf et al. (2002) and Arnold et al. (2002) has given the topic of surface biosignatures an empirical basis (see Red Edge Observations Within the Solar System for more details). In addition to the observational studies of Woolf et al. (2002) and Arnold et al. (2002), there have been theoretical discussion papers about surface biosignatures. Wolstencroft and Raven (2002)

have given a detailed discussion of the likelihood that O₂-producing photosynthesis will develop on Earth-like extrasolar planets. They considered chemical, astrophysical, climatological, and evolutionary processes to explore extrasolar photosynthetic mechanisms and detectability. They concluded that, despite many uncertainties and alternate possibilities, photosynthesis is likely to develop on many Earth-like planets and that its mechanism might well be identical to terrestrial photosynthesis. The exception is planets orbiting stars much cooler than the Sun; in this case they postulated mechanisms able to employ lower-energy photons via multiple photon photochemical processes would still allow photosynthesis, with the three- or four-photon process photosynthesis implying a red edge at longer wavelengths. Primarily because of skepticism about the practicality of a TPF-type mission in the optical and near-IR spectral bands, they concluded that detection of a red edge spectroscopic feature is impractical and that atmospheric oxygen is a much more promising photosynthesis biosignature. Knacke (2003) focused on the spectroscopic detection of microbial life. Single-celled microbial life is the dominant portion of Earth's biomass today (Madigan et al., 2002), and for the majority of time of life on Earth microbial life was the only life on Earth. [Microbial cell numbers on Earth are estimated to be on the order of 5×10^{30} , with the total amount of carbon in these cells equal to that in all plants on Earth, and the total nitrogen and phosphorus content 10 times that of all plant biomass (Madigan et al., 2002).] On Earth, microbe colonies form large aggregates in oceans (and sometimes on land); algae and plankton colonies have spectroscopic features due to chlorophylls and related photosynthetic pigments. Knacke (2003) pointed out, however, that visible wavelength microbial signatures are confused by the much stronger atmospheric reflectance and that any red edge feature redward of 600-700 nm would be extremely weak because of the high opacity of seawater at those wavelengths. Techniques to detect microbial life will be essential if microbial life is common, but multicellular life is rare in extraterrestrial environments. The best chance for detection and study of microbes will be with post-TPF/Darwin-type missions.

For the purposes of this paper we assume that it will be possible to carry out a TPF-like space mission at visible to near-IR (700–2,000 nm) wavelengths either in the next decade or at some

later time. We believe that searching for spectroscopic signatures of light-harvesting organisms (*i.e.*, spectroscopically resembling terrestrial plants) is an exciting science goal that will be carried out for at least some TPF targets.

The vegetation red edge feature's relevance and usefulness as a surface biosignature for astrobiological studies remain open to question and are the topics of this paper [see also the conference proceedings by Seager and Ford (2005) for a preliminary discussion]. In Earth's Vegetation Red Edge Spectral Feature we summarize relevant current knowledge of the red edge as it occurs in terrestrial vegetation, including its physical origin. Red Edge Observations Within the Solar System briefly reviews early attempts to search for vegetation on Mars via spectroscopic signatures and recent reports of detection of the red edge in Earthshine. The role of temporal variability in the detection of surface biosignatures is described in Using Temporal Variability to Detect Surface Biosignatures. Observations of Earthshine features are also reported in Using Temporal Variability to Detect Surface Biosignatures, including temporal behavior that supports the identification of the observed spectroscopic feature with plants on Earth's surface. In Extrasolar Plants we speculatively, but critically, consider the likelihood that the same red edge feature seen on Earth would occur for vegetation on another world. In False-Positive Mineral Reflectance Edges we point out the possibility of confusion of the vegetation red edge reflectance feature with mineral edge reflectance features. Finally, we draw some tentative conclusions in Summary and Conclusion.

EARTH'S VEGETATION RED EDGE SPECTRAL FEATURE

Empirical characteristics

Land-based chlorophyll-producing vegetation has a very strong rise in reflectivity at around 700 nm by a factor of 5 or more. This "red edge" spectral signature is much larger than the familiar chlorophyll reflectivity bump at 500 nm, which gives vegetation its green color. Figure 1 shows a deciduous plant leaf reflection spectrum (Clark *et al.*, 1993). The high absorptance at ultraviolet (UV) wavelengths (data not shown) and at visible wavelengths is by chlorophyll and is used by

the leaf for photosynthesis. Photosynthesis is the process by which plants and some other organisms use energy from the sun to convert H_2O and CO_2 into sugars and O_2 . The primary molecules that absorb the light energy and convert it into a form that can drive this reaction are chlorophyll A (absorption maxima in diethyl ether at \sim 430 nm and 662 nm) and chlorophyll B (absorption maxima in diethyl ether at \sim 453 nm and 642 nm).

A deciduous plant leaf is strongly reflective between 700 nm and 1,000 nm. [If human vision were sensitive a little further toward the red, the natural world would be very different in appearance: Plants would be very red and exceedingly bright (see Fig. 2).] Figure 2 shows that the leaf also has a very high transmittance at these same wavelengths, such that reflectivity plus transparency is near 100% at near-IR wavelengths. Remarkably, about 40% of the energy in solar radiation (Fig. 3) is at approximately 600– 1,100 nm—the same wavelength region where the deciduous leaf reflects or transmits almost all of the solar radiation (Gates et al., 1965). The exact wavelength and strength of the red edge depend on the plant species and environment. Although they are negligible from the biosignature detection view point, it is interesting to note that the specific wavelength dependence and strength of the red edge feature are used for remote sensing of specific locations on Earth to identify plant species and also to monitor a field of vegetation's (such as crops) health and growth as the red edge changes during the growing season. It is also useful to note that even conifers and desert plants have similar red edge features (see Clark et al.,

In the near-IR (Fig. 1), plants also have water absorption bands. The band strength depends on plant water content, weather conditions, plant type, and geographical region. These absorption features can be strong, on the order of 20% for the water bands at 1.4 and 1.9 μ m, but are not very useful for identifying life, since they would only be indicative of water and would likely not be distinguishable from atmospheric water vapor.

Ocean plankton blooms near coastal shores are colorful and large scale (*e.g.*, Behrenfeld *et al.*, 2001; Knacke, 2003). The color change in plankton blooms are due to the increased presence of chlorophyll—causing the presence of the 500 nm reflectance peak. Unfortunately, the change in intensity is small for a spatially unresolved extra-

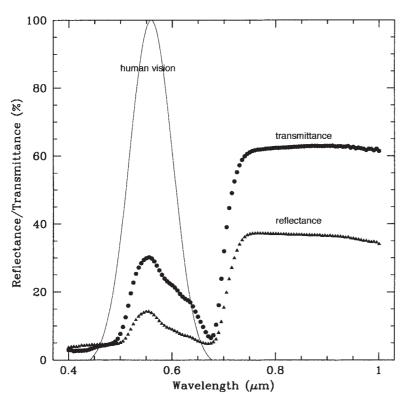


FIG. 2. Reflectance and transmittance of a young aspen leaf (data from Middleton and Sullivan, 2000). The reflection and transmittance curves are very similar, supporting the point that radiation keeps scattering until it exits the top surface or bottom surface of the leaf, except at pigment-absorbing wavelengths. Also shown is the normalized human vision response curve, which shows the non-sensitivity of humans to the vegetation red edge reflectance.

solar planet, especially when considering the low reflectivity of Earth's oceans and the small area of plankton blooms compared with a large part of a hemisphere.

Physical nature

A typical plant leaf spectrum exhibits the two different behaviors of leaves: a strong absorption in the visible, and high scattering (transmission + reflection) in the very-near-IR (750–1,300 nm), sometimes called the "red edge" or "IR plateau" by vegetation remote sensing experts (Fig. 2). The large-scale physical structure of leaves (the layers of cells and gaps between them) promotes scattering and therefore within a plant leaf absorption only occurs at wavelengths where specific chemical pigments or molecules absorb light. The visible-wavelength absorbers are determined to be chlorophylls or other pigments experimentally: In "variegated" plant leaves (leaves that are both green and white) the white part of the leaf has a reflectance as high in the visible as at near-IR wavelengths, and chlorophyll pigments are very absorptive at visible wavelengths but are not at all absorptive at near-IR wavelengths (Knipling, 1970, and references therein). Water absorbs portions of the near-IR reflectance spectrum. The wavelengths of water absorption bands are well known, and confirmation of water as the near-IR absorber has been shown with dehydrated leaves, which have a much higher near-IR reflectance spectra than hydrated leaves (Knipling, 1970).

Plant leaves are highly reflective in the spectral range 750 to 1,300 nm; few substances in nature reach this level of reflectivity. The reason a plant leaf is so highly reflective (and transmittive) is due to the leaf construction-structures at all scales make light scattering highly efficient (see, e.g., Gates et al., 1965; Knipling, 1970). The inside of a leaf is made up of water-filled cells with air gaps surrounding the cells. Light reflects off of the cell walls but also refracts through cell walls from the surrounding air gaps between cells. Inside the cell, light keeps scattering (except at pigment-absorbing wavelengths) until it exits the cell. Two causes keep light scattering inside the cell. Primarily, the high change in the index of refraction (from 1.33 for water to 1.00 for air) makes efficient internal reflection inside the water-filled cells at the interface between cell walls and the surrounding air gaps. Secondarily, light will Mie or Rayleigh scatter off of the cell's organelles, which have sizes on the order of the wavelength of light. Conclusive evidence of the importance

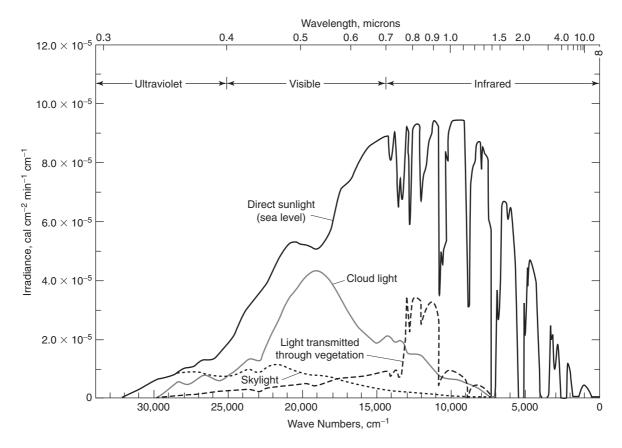


FIG. 3. Spectrum of solar flux that reaches the ground after absorption through Earth's atmosphere. Also shown is a representative curve for light transmitted through vegetation (light is reflected at the same wavelengths; see Fig. 2). Reproduced with permission from Gates *et al.* (1965). Vegetation reflects or transmits almost all incident radiation at wavelengths where sunlight has about 40% of its energy.

of the internal reflection to the plant leaf's high reflectance was shown by Knipling (1970). A water-infiltrated leaf with water filling the cavities between cells to form a continuous liquid water medium in the plant leaf has a high transmittance at the expense of lower reflectance. In other words, without internal reflection inside cells, most of the light entering the top of the leaf would travel down and exit out of the bottom leaf surface, but when cells are surrounded by an air gap a significant fraction of the incoming light is redirected upwards by repeated internal reflections. The leaf surface contributes only a small amount to reflectance (Knipling, 1970) by either specular reflection or scattered light. The amount of reflection depends on the presence of leaf surface wax [increasing reflection at visible (e.g., Grant, 1987) and near-IR wavelengths (e.g., Slaton et al., 2001)] and distribution, size, shape, and angles of any hairs present [either increasing or decreasing reflectance (Grant, 1987)]. Only at large angles of incidence is radiation predominantly reflected by

leaf surface specular reflection compared with leaf interior reflection (Grant, 1987).

Eventually, the radiation will scatter out of the leaf—designated "reflected" at the top or "transmitted" at the bottom. To support the explanation that radiation is scattered or transmitted everywhere except at wavelengths with absorption, Fig. 2 shows that a leaf's reflectance and transmittance spectrum are very similar. The magnitude, wavelength dependence, and ratio of the reflectance and transmittance are a complex function of the cell size and shape and the size and shape of the air gaps between the cells and hence depend on plant type. Three-dimensional Monte Carlo simulations are able to reproduce reflection and transmission spectral properties of plant leaves (*e.g.*, Govaerts *et al.*, 1996).

The overall reflectance of a plant is lowered by the plant canopy. The canopy effects include leaf orientation, shadows, and non-foliage background surfaces such as soil (Knipling, 1970). Leaf orientation, or specifically the angle of inci-

dence and reflectance of radiation, is important since leaves scatter light anisotropically. The canopy reduces reflection at visible wavelengths by approximately twice as much as it reduces reflection at near-IR wavelengths compared with a single leaf (by $\sim 40\%$ and $\sim 70\%$, respectively). This effect actually enhances the red edge amplitude and is due to the near-IR incident radiation reflecting off of lower leaves and retransmitting upward through upper leaves.

The high ratio of absorbed to scattered (reflected + transmitted) radiation on either side of the red edge is not fully understood. One explanation uses environmental adaptation. If plants absorbed solar radiation with the same efficiency at longer wavelengths than the red edge compared with visible wavelengths, then the plants would become too warm, and the proteins would be irreversibly damaged (Gates et al., 1965). Benedict and Gates (1963) have shown that approximately 75% of the total energy absorbed by plants is re-radiated, while approximately 25% is dissipated by convection and transpiration. Therefore, although thermal regulation is partially controlled by leaf stomata and water vapor content, radiation balance must also play a role in thermal regulation. It is likely that a plant balances the competing requirements of absorption of sunlight at wavelengths appropriate for photosynthesis reactions with efficient reflectance at other wavelengths to avoid overheating (Gates et al., 1965). Alternate to the environment adapation argument is an argument that the cell spacings that cause the high near-IR reflectance evolved for reasons other than thermal balance. The large intercellular spaces aid gas exchange (Konrad et al., 2000) and increase the absorption of photosynthetically active radiation (DeLucia et al., 1996). The thermal regulation argument is further weakened by the belief that higher plants evolved from aquatic ancestors; aquatic vegetation is less subject to overheating because of close thermal coupling with the ambient water.

RED EDGE OBSERVATIONS WITHIN THE SOLAR SYSTEM

Spectroscopic searches for vegetation on Mars

During the early part of the last century, speculation about vegetation on Mars was fueled by reports of a wave of darkening that appeared dur-

ing many martian springs (Lowell, 1911; Sinton, 1958, and references therein). This wave of darkening changed large dull-colored regions to darkish-green hues and proceeded from pole to equator within a few weeks of the disappearance of the polar caps. The proposed explanation was that the vegetation was nourished by the melting polar snow. Although other explanations were put forth, for proponents of life on Mars the vegetation theory was second in popularity only to the martian canals. Because the spectrum of vegetation (Fig. 1) is different from other green materials, remote sensing was used to test Earth-like vegetation hypothesis. By taking spectra of different areas of Mars with a large telescope (72 inches), Millman (1939) was able to rule out Earth-like vegetation based on measurements of the absence of a 500 nm chlorophyll bump. Others used the red edge reflectance to rule out the vegetation hypothesis (Slipher, 1924; Tickhov, 1947; Kuiper, 1949). Later it was shown that the darkening on Mars was caused by changes due to windblown dust (Sagan and Pollack, 1969, and references therein).

In the 1950s new excitement and controversy arose from the claim of Sinton (1957) of evidence for vegetation on Mars. Sinton observed near-IR absorption features of organic molecules that were also observed to be present in lichen and some dried plants. Specifically, the C-H vibration bands occur in the 3–4 μ m region. Sinton argued that Mars may have vegetation similar to the hardiest vegetation on Earth: lichens (a symbiosis of fungi and algae). Lichens show the C-H near-IR absorption bands but lack the red edge vegetation spectrum even though they carry out photosynthesis. This theory of vegetation on Mars was ruled out in the early 1960s when two of the observed C-H absorption bands were identified as deuterated water in Earth's atmosphere (Rea et al., 1965).

Observing Earth as a reference case extrasolar planet

Because Earth is the only planet known to harbor life, it is the obvious and only test case of techniques for the search for life on extrasolar planets.

Sagan *et al.* (1993) used the Galileo spacecraft for a "control experiment" to search for life on Earth using only conclusions derived from data and first principle assumptions. En route to Jupiter, the Galileo spacecraft used two gravita-

tional assists at Earth (and one at Venus). During the December 1990 fly-by of Earth, the Galileo spacecraft took low-resolution spectra of different areas of Earth. In addition to finding "abundant gaseous oxygen and atmospheric methane in extreme thermodynamic disequilibrium," Sagan et al. (1993) found "a widely distributed surface pigment with a sharp absorption edge in the red part of the visible spectrum" that "is inconsistent with all likely rock and soil types." When an observer examined ~100-km² areas of Earth's surface, the vegetation red edge feature showed up as a reflectance increase of a factor of 2.5 between a band centered at 670 nm and one at 760 nm. In contrast, there was no red edge signature from non-vegetated areas.

A new technique for observing Earth as an extrasolar planet test case is now emerging: using Earthshine to study the spatially unresolved Earth. These studies are similar to those of Sagan et al. (1993), but they utilize Earth's spatially integrated light as if Earth were a point source, instead of areas of 100 km². Earthshine is sunlight that has been scattered by Earth toward the Moon and then back to Earth. It is often visible as a faint glow on the otherwise dark region of the lunar disk during crescent phases. Earthshine can be studied with a charge-coupled device (CCD) camera and specialized coronagraph even as the Moon waxes (Goode et al., 2001). The very rough lunar surface makes the Moon a diffuse reflector with each point on the Moon reflecting the spatially integrated illumination from Earth. The viewing geometry of Earth is the sunlit illuminated portion of Earth as seen from the Moon. A prescient paper by Arcichovsky (1912) proposed looking for vegetation signatures in Earthshine as a reference case for vegetation or chlorophyll searches on other planets. So, while activity and progress in Earthshine research are recent, the idea itself is an old one.

Earthshine observations can provide a valuable complement to existing satellite data sets that have been obtained for a wide variety of purposes and with diverse instruments. Since most satellite data are collected by looking nearly straight down at limited regions of Earth's surface and most often with relatively direct solar illumination angles, derivation of the integrated spectrum of the unresolved Earth with its varying atmospheric path lengths and solar illumination angles is not generally possible. Moreover, many satellite observations are obtained without attention

to absolute flux calibration (because it is not necessary to the purposes for which the data were obtained) and thus cannot be combined with other data to derive an integrated spectrum. Thus, for the purpose of time domain comparisons of the unresolved Earth's spatially integrated spectrum, Earthshine provides the best currently available information.

Recent spectral observations of Earthshine have tentatively detected the red edge feature at the 4–10% level. Woolf et al. (2002) observed the setting crescent moon from Arizona, which corresponds to Earth as viewed over the Pacific Ocean. Nevertheless, their spectrum (Fig. 2 in Woolf et al., 2002) shows a tantalizing rise just redward of 700 nm, which they tentatively identify with the red edge feature. The same figure also shows other interesting features of Earth's visible-wavelength spectrum, notably O₂ and H₂O absorption bands (note that spectral lines of both O_2 and H_2O cut into the red edge signature.) Arnold et al. (2002) made observations of Earthshine on several different dates. With observations from France, Earthshine on the evening crescent moon is from America and the Atlantic Ocean, whereas Earthshine on the morning crescent moon is from Europe and Asia. After subtracting Earth's atmospheric spectrum to remove the contaminating atmospheric absorption bands, they found a vegetation red edge signal of 4–10%. However, note that it will be extremely difficult to subtract an unknown extrasolar planet's atmospheric spectrum in the kind of low-signal-tonoise data expected with the future space missions TPF and Darwin.

An alien civilization observing the spatially unresolved Earth with a TPF-like telescope would have difficulty in identifying the vegetation red edge signature in medium spectral resolution data. While the red edge spectroscopic feature is very strong for an individual plant leaf, at a factor of 5 or more, it is much reduced—down to several percent—when averaged over a (spatially unresolved) hemisphere of Earth. This is due to several effects, including extremely large vegetation-free regions of Earth's surface, the presence of clouds that block sight lines to the surface, anisotropic scattering by vegetation canopies, and soil characteristics. In addition, the reflectance of vegetation is anisotropic, so the illumination conditions and planet viewing angle are important. Nevertheless, at a signal level of a few to several percent, Earth's vegetation red edge is

still a viable surface biosignature for a TPF-like mission. In favorable hypothetical cases, however, the feature could be much stronger than the ones so far observed in Earthshine. For example, if the planet cloud-cover fraction is lower, a larger fraction of the surface is covered by vegetation, or a smaller fraction of the illuminated portion of the planet is visible (*i.e.*, a crescent phase) the fractional amplitude of the red edge would be increased in the integrated spectrum.

In contrast to the red edge signature, the chlorophyll bump at 500 nm is extremely small in a hemispherically averaged spectrum of Earth. The spectral signature of oceanic vegetation or plankton is also unlikely to be detectable with TPF/Darwin-generation telescopes because of strong absorption by particles in the water and the strong absorptive nature of liquid water at red wavelengths (see Knacke, 2003). In the next section we argue that temporal variability may be key for detection of weak but changing surface features such as the vegetation red edge feature.

USING TEMPORAL VARIABILITY TO DETECT SURFACE BIOSIGNATURES

A time series of data in different bands should help make it possible to detect a small but unusual spectral feature, even with variable atmospheric features. As the continents rotate in and out of view, a planet's brightness, colors, and spectrum will change. Most of Earth's surface features, such as sand or ice, have a continuous or minimal change in albedo with wavelength, in contrast to the abrupt vegetation red edge spectral feature.

We have shown (Ford *et al.*, 2001) via simulations that the existence of different surface features on a planet may be discernible at visible wavelengths as different surface features rotate in and out of view. Considering a cloud-free Earth, the diurnal flux variation caused by different surface features could be as high as 200%. This high flux variation is not only due to the high contrast in different surface components' albedos, but also to the fact that a relatively small part of the visible hemisphere dominates the total flux from a spatially unresolved planet. Clouds increase Earth's albedo, interfere with surface visibility, and reduce the fractional amplitude of the diurnal light curve to roughly ~10–20%. Because

cloud cover is stable for days over some regions, the rotational period of Earth could still be measured (Ford *et al.*, 2001).

We here restrict our attention to diurnal time scales. However, any vegetation indicator might also display seasonal (on an orbital timescale) variations. In this section we describe Earthshine observations from two different Earth–Moon geometries made to detect temporal variation of the vegetation red edge signature.

Apache Point Observatory (APO) Earthshine observations

Spectra of Earthshine were obtained with the Double Imaging Spectrograph (DIS) on the APO 3.5-m telescope (which is owned and operated in New Mexico by the Astrophysical Research Consortium) between 11:30 and 13:00 on 8 February 2002 (Universal Time) with the Moon rising in the eastern sky and again between 01:00 and 01:30 on 16 February 2002 (Universal Time) with the Moon setting in the western sky. As shown in Fig. 4, the dark side of the Moon was illuminated by light scattered from quite different portions of Earth's surface on the two dates. About 20% of the visible portion of the Moon's surface was illuminated by sunlight on 8 February 2002 and about 10% on 16 February 2002. Airmass was necessarily high for both sets of observations, ranging from approximately 3 to 7, the latter being the approximate elevation limit of the telescope. The same spectroscopic setup was used on both dates; in particular a 150 lines/mm red blazed grating was used to obtain spectra of approximately 10 Å resolution with a 1.2 arcsec by 5 arcmin "bar slit." Although the whole range from about 400 to 1,000 nm was observed, we here concern ourselves only with the 600-900 nm range, roughly centered on the red edge feature and in which a relatively clean and high signal-to-noise spectrum could be extracted. The detector was an unthinned, and thus relatively unaffected by CCD fringing, 800×800 TI device.

During the 8 February 2002 observations, eight exposures were obtained of the dark limb of the Moon (*i.e.*, Earthshine illuminated limb), followed by three exposures of a sunlit mountain peak just on the dark side of the lunar terminator, and then followed by seven more exposures on the dark limb. On 16 February 2002, because of a much shorter total available observing time, only four dark limb and one sunlit mountain top

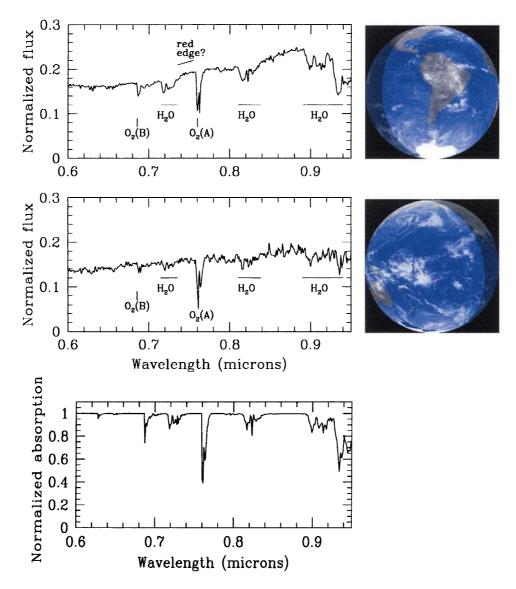


FIG. 4. Earthshine observations from APO. Top panel: Earthshine observations on 8 February 2002. The viewing geometry (including cloud coverage at the time of observations) of Earth from the Moon is shown in the right image (http://www.fourmilab.ch/earthview/vplanet.html). **Middle panel:** Same as the top panel for 16 February 2002. The viewing geometry of Earth includes much more vegetation in the top panel than in the middle panel. **Bottom panel:** An absorption spectrum through Earth's atmosphere from Kitt Peak National Observatory (ftp://ftp. noao.edu/catalogs/atmospheric/transmission/) smoothed to approximately the same resolution as the APO Earthshine data. Note the different *y*-axis on the absorption spectrum; the spectral features are much deeper than in the Earthshine spectrum, and there is no red edge feature.

exposures were obtained. Dark limb exposures were made with the slit approximately centered on and perpendicular to the limb, so as to obtain both an Earthshine signal and a sky spectrum. Typical exposure times were 60 s on the dark limb and 10 s on the sunlit mountain peaks. Exposures with the "slit viewer" target acquisition camera indicated that it would be impossible to obtain DIS exposures of the fully sunlight illuminated bright limb without saturating the detector, even

with the shortest available shutter times; the availability of small (spatially unresolved) areas of sunlit lunar surface on mountain tops just beyond the terminator nevertheless enabled us to obtain high signal-to-noise bright-side spectra well within the CCD detector's linear response regime.

The data reduction and extraction of Earthshine spectra followed the general technique and procedures of Woolf *et al.* (2002) and Arnold *et*

al. (2002), who first reported the possible detection of the red edge feature in an Earthshine spectrum. Standard Image Reduction and Analysis Facility image processing and spectral reduction routines were used with the exception of sky subtraction for the dark limb exposures, as described below. First, standard bias frame subtraction and flat fielding corrections were carried out for each exposure. A sky contribution to the dark limb spectra was determined by a linear extrapolation of the observed sky counts at each wavelength to each position along the part of the slit positioned on the lunar surface. Visual examination of the sky counts versus position along the slit beyond the lunar limb established that the linear extrapolation was an adequate representation of the spatial variation of sky brightness due to scattering from the nearby (in the sky) bright lunar crescent. Sky subtraction for the bright-side spectra was made in the conventional way by subtracting an interpolation between the dark areas on either side of the sunlit mountain peaks but was in any case so small as to be insignificant. The resulting dark limb spectra were then averaged over about 30 arcsec of the slit's length across the lunar surface, both to improve signalto-noise and to average out any fluctuations in the wavelength dependence of the lunar albedo (*i.e.*, changes in the color of the lunar surface). Unfortunately, no such averaging was possible of the spectra of the lunar mountain tops, and as a result, any difference between their wavelength-dependent albedo and that of the averaged areas observed on the dark limb will appear as systematic noise and, perhaps, a spurious feature in our final Earthshine spectra. Finally, the spectra of the dark limb were divided by those of the sunlit mountain peaks and averaged together to give a spectrum of Earthshine that illuminated the dark side of the Moon on each of the two dates. These are shown in Fig. 4 along with a representation of Earth as it appeared from the Moon (see http://www.fourmilab.ch/ earthview/vplanet.html) at the times of the observations. The nominal signal-to-noise ratio of these spectra is in the range of 30–100 per resolution element with a significant contribution from high-spatial-frequency CCD flat field features, but the true uncertainty in these spectral measurements is almost certainly dominated by potential systematic errors discussed in the next section.

Interpretation of APO Earthshine spectra

The most important conclusion to be drawn from the spectra shown in Fig. 4 is that they appear to confirm the tentative identification of the 700–750 nm feature seen in Earthshine spectra of Woolf et al. (2002) and Arnold et al. (2002) as actually being due to the red edge in the spectral reflectance curves of the leaves of deciduous terrestrial plants. This conclusion is based on the fact that a similar feature to the Woolf et al. (2002) and Arnold et al. (2002) feature occurs in our "vegetation-covered" Earth spectrum but not in our non-vegetation-covered Earth spectrum. In our vegetation-covered spectrum from 8 February 2002, the Moon was illuminated by light scattered from large land areas that are covered by heavy vegetation—most notably the extensive forests of South America. In our non-vegetation-covered spectrum of 16 February 2002, the Moon was primarily illuminated by light scattered off of parts of Earth's surface that contain no deciduous vegetation—primarily the South Pacific Ocean. Thus, at a crude and qualitative level at least, the presence and absence of the red edge feature correlate with the presence and absence of large quantities of plant life in the sunlight-illuminated portion of Earth as seen from the Moon.

Spectral slope is routinely used to quantify detections of the red edge via satellite observations of Earth. In the vegetation-covered APO spectrum, the continuum level of Earthshine rises by $17 \pm 2\%$ between 700 and 750 nm. In contrast, the non-vegetation-covered APO Earthshine spectrum has an increase of only $11 \pm 2\%$ over the same wavelength range. [M. Turnbull et al. (manuscript in preparation) suggest that the gradual increase in slope of the spectra throughout the entire wavelength range is due to the difference in lunar albedo as a function of phase angle; the dark part of the moon is illuminated by Earthshine at a phase angle roughly near 10°, whereas the bright crescent moon is illuminated by the sun closer to 170°.] These values appear plausibly consistent with the 6% increase reported by Woolf et al. (2002) and of 4–10% reported by Arnold et al. (2002) in spectra of Earthshine produced by light scattered from various other parts of Earth's surface.

The change in the slope of the continuum in the vegetation-covered case is even more striking; the slope is 14 ± 3 times larger between 700

and 750 nm than between 650 and 700 nm! This abrupt break corresponds to the ramp-like appearance of the continuum at the red edge location in the 8 February spectrum shown in Fig. 4. The non-vegetation-covered spectrum also shows a mild reddening of the continuum slope, by a factor of about 2.5 ± 0.5 , in a comparison of the same two wavelength intervals. This much smaller feature could be due to a minor red edge contribution to Earthshine from plants near the illuminated limb of Earth (as seen from the Moon), but it is not significantly bigger than changes in the continuum slope at other wavelengths due to gentle bumps and dips in the spectrum's overall shape. Thus, we cannot claim secure detection of any feature at the red edge location in the 16 February data.

Although a more quantitative comparison of the expected and observed strength of the feature would be possible via calculations such as those reported by Ford et al. (2001), we do not believe that the quality and limited quantity of the currently available data justify such a comparison. However, it is clear that a more well-developed data set of Earthshine spectra, taken at different moon phases and times (seasons), as well as from different locations on Earth's surface, could unambiguously establish the association of the 0.75 μ m feature with the red edge of vegetation, as well as document its variability. Such data would also be very useful for purposes of testing and validating models of Earth's photometric properties such as that developed by Ford *et al.* (2001).

The spectra shown in Fig. 4 display two additional characteristics that merit comment: (1) a variation in the strength of the water vapor lines between the 8 February and 16 February 2002 spectra and (2) another strong increase in brightness around a wavelength of 850 nm.

The water vapor line variability is likely due to differences in the average water vapor column density in Earth's atmosphere over the illuminated regions on the two different dates of observation (see Fig. 4). We note that the water vapor features do not show any systematic variation with airmass in subsets of the spectra obtained on either date. We caution, however, that there is a small chance that the water variation may nevertheless reflect imperfect cancellation or removal of the atmospheric water vapor in front of the telescope during the observations due, perhaps, to the high and rapidly changing airmass through

which the observations were necessarily obtained.

We have found no plausible explanation for the 850 nm feature; it could be real and deserving of further investigation. It might also be artificial in the sense of arising not on Earth but from the Moon; in other words, it might be due to a variation in the color of the lunar surface between the regions where the dark limb and the sunlit surface spectra were obtained, as described above in the Apache Point Observatory (APO) Earthshine observations section. Any such difference would not be removed by the division of the dark by the bright-side spectra. We note, however, that Earthbased (McCord et al., 1972) and spacecraft (see http://vims.artov.rm.cnr.it/data/res-moo.html) measurements of the wavelength dependence of the albedo of lunar highland regions do not show any strong features at either the position of the red edge or near 850 nm. Whether the 850 nm feature is created at Earth or on the Moon, it warns of the difficulties that may arise when searching for red edge-like spectral features on other planets. We note that Earthshine spectrum by Woolf et al. (2002) shows a 7% decrease (approximately three times smaller change than we see at 850 nm) at wavelengths ~780 nm and longer. M. Turnbull et al. (manuscript in preparation) also see a depression in their reflectance spectra at similar wavelengths.

These systematic uncertainties are not only relevant to the particular data presented here but also illustrate some of the intrinsic challenges of Earthshine observations using general purpose telescopes and instruments. The sunlit and Earthshine illuminated portions of the lunar disk differ in surface brightness by at least on the order of 10⁴ and are thus very difficult to observe with comparable signal-to-noise using the same equipment and instrumental configuration. Moreover, rapidly changing airmass and a very limited period of time available for the whole sequence of exposures are unavoidable consequences of observing a crescent moon from observatories at mid-latitudes. These time constraints make it impractical to reconfigure the instrumentation repeatedly to facilitate observations of the bright and dim portions of the lunar surface, e.g., by insertion and removal of a pupil plane diaphragm or a neutral density filter in a spectrograph that was not designed with such operations in mind. And, of course, the high airmasses associated

with crescent moon configurations are directly problematic; they change significantly over a few minutes and thus even during and between fairly short exposures. Earthshine spectroscopy using special purpose instruments or instrument configurations either from polar regions of Earth (S. Kilston, personal communication, 2002) or orbiting telescopes (Davis *et al.*, 2002; N. Woolf, personal communication, 2001) could circumvent these difficulties.

EXTRASOLAR PLANTS

The red edge will only be a useful tool for astrobiology if extrasolar vegetation also exhibits a similar extraordinary spectral signature. We have no firm basis for believing in the existence of extrasolar vegetation. It is nevertheless essential to keep in mind that the situation is qualitatively the same for every technique that can be used for the search for life in the Universe. Absent a fundamental, first principles understanding of biology that could predict what is possible and likely, we are forced to assume that extraterrestrial life resembles life on Earth to some degree. Assuming that extraterrestrial life has nothing at all in common with terrestrial organisms makes searching for it almost impossible. The opposite extreme of assuming that terrestrial life and extraterrestrial life are exactly identical is simplistic and would lead to such narrowly focused search techniques that would risk missing most actual indications of extraterrestrial biology.

In this section, we offer some of the relevant facts and arguments to inform the required educated guess. This is in contrast to Wolstencroft and Raven (2002), who used details of the photosynthesis mechanism to argue that the evolution of O₂-producing photosynthesis is likely on extrasolar Earth-like planets. A few interesting points concerning terrestrial vegetation are useful for speculating on the possible existence of extrasolar plants or "light-harvesting organisms" and potential magnitude of spectral features:

 Plants absorb very strongly throughout the UV (at wavelengths longer than 380 nm) and the visible wavelength regions of the spectrum where photon energies are sufficient to drive photosynthesis (involving molecular electronic transitions). • Plants reflect and transmit almost 100% of light in the wavelength region where the direct sunlight incident on plants has about 40% of its energy (Gates *et al.*, 1965).

- Considering the above two points, Earth's primary surface "light-harvesting organism," vegetation, may have evolved to balance the competing requirements of absorption of sunlight at wavelengths appropriate for photosynthesis reactions with efficient reflectance at other wavelengths to avoid overheating (Gates et al., 1965). The prime selective factor in evolution, however, is not known, and vegetation's high reflectance and transmittance may instead have been selected for other traits, namely, the large intercellular gas spaces aiding gas exchange (Konrad et al., 2000) and increasing the absorption of photosynthetically active radiation (DeLucia et al., 1996). Regardless of the evolutionary origin, the high reflection may be key to vegetation's survival on land.
- In addition to chlorophyll, many other lightabsorbing pigments exist. Accessory pigments at different wavelengths (Fig. 5) absorb photons and transfer energy to chlorophyll a. These accessory pigments allow photosynthetic organisms to use a wide range of wavelengths of light. Specifically, chlorophyll a is found in all photosynthetic organisms except some photosynthetic bacteria, chlorophyll b is found in higher plants and green algae, accessory pigment β -carotene is found in all photosynthetic organisms except photosynthetic bacteria, and phycoerythrin and phycocynanin (phycobilins) are found in red algae and cyanobacteria, respectively. In addition to the variety of accessory pigments, the chlorophyll pigment itself comes in different forms with absorption maxima at different wavelengths. For example, photosynthetic bacteria (both aerobic and anaerobic) have bacteriochlorophyll pigments (Fig. 5). The wavelength variation in the pigments makes some organisms better adapted to their ecological niches. For example, cyanobacteria (chlorophyll a and phycocyanin) in lakes and ponds often form a dense surface layer, absorbing a large amount of blue and red light. Purple photosynthetic bacteria (bacteriochlorophyll a or b) and green photosynthetic bacteria (major pigment is bacteriochlorophyll c, d, or e) grow best in anaerobic conditions in deep water. At depth, the previ-

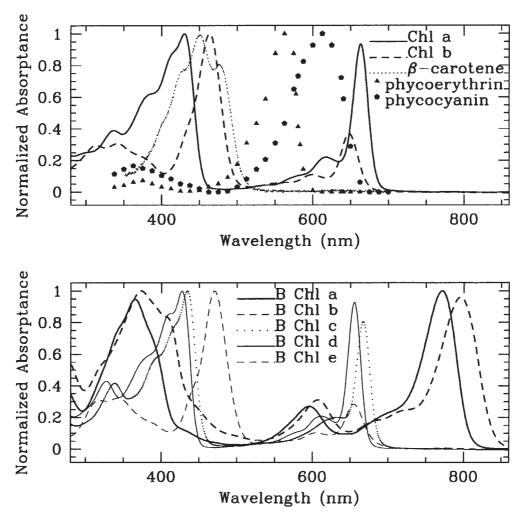


FIG. 5. Wavelength dependence of some of the pigments involved in photosynthesis. Top panel: Chlorophyll (Chl) a and b [dissolved in a solution of methanol, acetonitrile, ethyl acetate, and water (Frigaard et~al., 1996)]; accessory pigment β-carotene [dissolved in hexane (Du et~al., 1998)]; accessory pigments phycoerythrin and phycocynanin [dissolved in water (Purves et~al., 1995)]. Bottom panel: Wavelength dependence of bacteriochlorophyll (B Chl) pigments. The B Chls are found in photosynthetic bacteria. The data plotted here are pigments dissolved in a solution of methanol, acetonitrile, ethyl acetate, and water. Data courtesy of Niels-Ulrik Frigaard (Frigaard et~al., 1996). See Extrasolar Plants for discussion.

ously cyanobacteria-absorbed blue and red light is not available. The bacteriochlorophyll pigments allow the purple and green bacteria to take advantage of their ecological niche in deep water by absorption of longer wavelength light. In addition, bacteriochlorophyll a and b have absorption maxima at shorter wavelengths than chlorophyll a, taking advantage of the deep water where shorter wavelength light can penetrate water farther.

 While vegetation and other organisms use chlorophyll pigments to convert light to energy, there exists at least one alternate photosynthetic system using an independent pigment, rhodopsin. Bacteriorhodopsin (a type of rhodopsin) occurs in halobacteria (Oesterhelt and Stoeckenius, 1971) found in highly salty environments, for example, in the Dead Sea. Proteorhodopsin is found in marine bacterioplankton that are widespread in the surface ocean (Beja *et al.*, 2001). The rhodopsin photosynthetic system is chemically fundamentally different from the chlorophyll photosynthetic system.

If we accept that extraterrestrial light-harvesting organisms should be ubiquitous, would they likely have a strong spectroscopic signature?

Light-harvesting organisms may have properties similar to those of vegetation in order to absorb the correct frequency energy for molecular transitions but not absorb all available energy. Light-harvesting pigments in vegetation cover the full range of the visible-light spectrum, and many of these pigments have sharp spectral features at the red edge of the pigment's absorbing range (Fig. 5). Thus, extrasolar light-harvesting organisms may have sharp spectral features similar to terrestrial vegetation's red edge spectral feature but at different wavelengths.

In some cases, light-harvesting organisms might have no strong spectroscopic signature. For example, a hypothetical light-harvesting organism that is absorptive at short visible wavelengths but purely transmissive at red and near-IR wavelengths would have no sharp spectroscopic features detectable by reflectance spectroscopy. A second example comes from terrestrial photosynthetic organisms. In addition to vegetation there is a large diversity of photosynthetic organisms (e.g., multicellular and unicellular algae and prokaryotic organisms such as cyanobacteria and green and purple bacteria). Over half the photosynthesis on Earth is carried out by microorganisms (Field et al., 1998). Many of these organisms live in water, and some carry out anoxygenic photosynthesis—any spectral biosignature would be weakened in the spatially integrated global spectrum because of the high opacity of ocean water.

We favor the opinion that light-harvesting organisms with pigments and spectral features at various wavelengths should be common over the idea that the red edge signature from terrestrial plants is widespread and universal (although the pigment "edge" may or may not be a sharp feature; see Fig. 5). Given the abundance and ready availability of low-entropy energy in the form of radiation from the primary star, assuming a sufficiently transparent atmosphere, "light-harvesting" is likely to be a common feature of life, simply because it is such an effective biological strategy. In other words, if such a beneficial mechanism develops in any organism, it seems likely to be subject to strong positive evolutionary selection. Wolstencroft and Raven (2002) also concluded that light-harvesting organisms with pigments and spectral features at different wavelengths should be common, by the different assumption that Earth-based photosynthesis should be common.

Evolution has an element of chance, and whatever light-harvesting mechanism develops first on a planet might be evolutionarily favored over other mechanisms that are theoretically more efficient. Thus, Earth-based photosynthesis is not necessarily the best or most efficient light-harvesting mechanism even for the conditions on Earth. Further, there is no compelling a priori reason to believe that organisms on other planets would independently develop a light-harvesting mechanism identical to the one found in terrestrial vegetation. Furthermore, many mechanisms evolved initially for other functions. For example, it has been suggested that chlorophyll arose from UV-screening cell-surface proteins (Mulkidjanian and Junge, 1997). The proteins that originally developed as a protective measure later evolved into using the absorbed radiation for energy. So, for example, organisms living on planets around stars cooler than the Sun may have pigments at slightly different wavelengths [see Wolstencroft and Raven (2002) for a discussion of O₂-producing photosynthesis around cool stars].

Our chain of reasoning does not lead to any definite conclusion; however, it does give us some basis for an opinion: A red edge-like spectroscopic signature, as a biosignature for astrobiology, is sufficiently promising to warrant the search for similar features in the spectra of extrasolar terrestrial planets using TPF-type and successor missions. If such a feature were detected with time variability and other systematic behaviors, we believe that it would be an extremely interesting clue that suggests the possible existence of light-harvesting organisms on the planet. On the other hand, we do not believe that a failure to detect a red edge-like signature in the spectrum of an extrasolar terrestrial planet would provide any meaningful null result with respect to life on the planet.

FALSE-POSITIVE MINERAL REFLECTANCE EDGES

Semiconductor crystals also have spectral reflectance "edges" at or near visible wavelengths (Fig. 6). The spectral reflectance edges are due to the valence electrons lacking available states for a certain range of energies. The semiconductor's band gap is the energy difference between the valence shell band and the conduction band. Photons with enough energy are

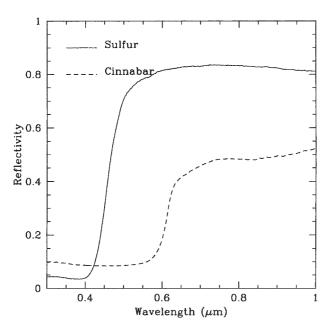


FIG. 6. Reflectance spectra of the minerals sulfur and cinnabar (from Clark *et al.*, 1993). Note the sharp edge features.

absorbed, since they can excite electrons from the valence band into the conduction band. Photons with energies less than the band gap, however, are absorbed and remitted with the same energy—i.e., scattered—by electrons within the valence band. At zero temperature, there is a sharp step function reflectance edge at the wavelength of the energy gap. At higher temperatures, the reflectance edge is smooth and sloped, since there is a chance that an incident photon will excite an electron already above the ground state and the combined energy will be sufficient for the electron to jump the band gap. For many semiconductors, the band gap energy corresponds to the energy of photons in the visible to near-IR portions of the spectrum. Therefore, mineral semiconductors will also have spectral reflectance edges at visible to near-infrared wavelengths. For example, cinnabar (HgS) is a mineral with a steep reflectance edge (Fig. 6) at red wavelengths (600 nm). It is important to remember that the band gap phenomenon is dependent on the crystalline structure of the semiconductor, which creates a periodic potential for the impinging photon. Thus, if the physical size of the crystal does not significantly exceed the wavelength of the incident photons, then the spectra can be significantly altered by the shape and size of the crystals. In the Solar System, most planetary surfaces are covered with a regolith

that complicates the interpretation of mineral reflectance spectra.

A planet with a lot of exposed rocks (aggregates of mineral) could potentially produce a strong mineral edge signature, even though most minerals do not exist in isolation on planetary surfaces. Like the vegetation edge, a mineral reflectance edge could vary as continents rotate in and out of view. A mineral edge detection would be interesting in and of itself. For example, a substantial fraction of Jupiter's moon Io is likely covered by solidified elemental sulfur allotropes (Moses and Nash, 1991) that originated from volcanic eruptions. Crystalline sulfur is an intermediate-energy band gap semiconductor and has a sharp reflectance edge at 450 nm (Fig. 6). Diskaveraged reflectance spectra of Io are remarkable in that blueward of the mineral edge Io's albedo is near zero and redward of the mineral edge the albedo is 0.8 (e.g., Spencer and Schneider, 1996).

If a reflectance edge were detected in the spectrum of an extrasolar terrestrial planet, then it would be important to consider all possible sources, including both mineral and biological. In particular, a careful study of mineral signatures and atmospheric composition will be necessary before attributing a spectral edge to a light-harvesting pigment. Although only a dozen or so rock-forming minerals are common on Earth, over 4,000 minerals are known. While their spectra can be measured in the laboratory and compared with the extrasolar planet reflectance spectrum, it can be tricky to identify a particular mineral from a reflectance spectrum (e.g., Moses and Nash, 1991). Additionally, the spectra of surfaces covered with a regolith of small particulate minerals can deviate significantly from laboratory spectra based on large crystals. Nevertheless, it may be possible to eliminate the possibility of some minerals based on additional measurements. For example, most minerals have near-IR and mid-IR (5–40 μ m) absorption features. Therefore, a mid-IR spectrum (e.g., from the mid-IR TPF/Darwin) at wavelengths where radiation penetrates to the planet's surface could help identify a mineral that covered a large fraction of a planet's surface. Measurements of atmospheric composition could also be valuable for ruling out certain minerals. For example, if a detected spectrum showed a significant amount of atmospheric oxygen, then non-oxidized minerals are unlikely to be abundant on the planetary surface. The wavelength of Earth's vegetation red edge does

not correspond to that of any known mineral (Sagan et al., 1993).

SUMMARY AND CONCLUSION

When extrasolar Earth-like planets are discovered, observations at wavelengths that penetrate to the planet's surface will be useful for detecting surface features, including biosignatures, especially for planets with much lower cloud cover than Earth's 50%. The vegetation red edge spectroscopic feature is a factor of 5 or more change in reflection at ~700 nm in deciduous plant leaves. This red edge feature is often used in remote sensing studies of Earth's vegetation. Earthshine observations have detected a feature identified with the red edge in the spatially unresolved spectrum of Earth where it appears at the few percent level. Earthshine observations reported here display the expected dependence of the feature on the portion of Earth both illuminated by sunlight and visible from the Moon, and thus support this interpretation.

Earth's hemispherically integrated vegetation red edge signature, however, is weak (a few percent to 10% vs. the ≥50% in leaf reflectance) because of dilution by other atmospheric (e.g., clouds) and surface (e.g., oceans and non-continuous forest coverage) features. The recent Earthshine measurements have confirmed the expected amplitude of the red edge signature, and show that its detection is non-trivial in Earth's spatially unresolved spectrum with current and near-future planned technology. Earth-like planets with different rotation rates, obliquities, higher land-ocean fraction, different continental arrangement, and lower cloud cover might well display a more easily detectable red edge-type signal.

A time series of spectra or broadband photometry will help to identify weak surface biosignatures such as the red edge-type feature in a spatially unresolved spectrum of an extrasolar planet. The new Earthshine observations reported here indicate just such temporal variability of Earth's red edge surface biosignature. The increased temporal variability at a carefully chosen color could make detection of such features easier. In particular, any changes associated with a rotational period would be highly relevant, but compare the section on False-Positive Mineral Reflectance Edges for a discussion of surface mineral false-positives.

Because the existence of extraterrestrial light-harvesting organisms is plausible, any prediction of the characteristics of light-harvesting organisms on extrasolar planets is highly speculative and uncertain. In particular, the wavelength of any surface biosignatures would not be known *a priori*. Therefore, flexible data acquisition will maximize scientific return from future missions. For example, spectra can be integrated into photometry in many possible different bands after the data are acquired. Similarly, a relatively high cadence of observations can later be searched for rotational periods associated with surface features.

The physical and evolutionary characteristics of the red edge and the biological significance of photosynthesis make it plausible that extraterrestrial organisms might use pigments to harvest light, and that these organisms might develop a red edge-like spectral feature to protect their pigments. If a red edge-like feature were detected in combination with the spectral signatures of biosignature gases, then it could be strongly suggestive of the presence of life on the planet. Moreover, the detection of any unusual spectral feature that is inconsistent with known atomic, molecular, or mineralogical signatures would be extremely interesting, and the fact that Earth's spectrum displays at least one such detectable feature of biological origin is encouraging. Combinations of unusual spectral features together with strong disequilibrium chemistry would be even more intriguing and would certainly motivate additional studies to better understand the prospects for such a planet to harbor life.

ACKNOWLEDGMENTS

We thank the members of the Princeton TPF group plus Steve Kilston, Wes Traub, and Nick Woolf for valuable discussions of the red edge and Earthshine. We also thank Mike Wevrick for useful contributions, Harold Morowitz, Andrew Steele, Jan Toporski, Maggie Turnbull, and Nancy Kiang for useful discussions about chlorophyll and leaf structure, Olga Degtyareva for translating the article by Arcichovsky (1912), Tom Murphy for providing specialized lunar pointing and tracking telescope control software, Merri Wolf for careful library research, and Gabriela Mallen-Ornelas for contributing APO observing time and for a careful reading of the manuscript. Russet

McMillan and Camron Hastings of APO supplied expert assistance with the somewhat unconventional demands of Earthshine observations using a large telescope and a faint object spectrograph. We thank the referees for valuable comments. S.S. is supported by the Carnegie Institution of Washington. This material is also based upon work supported by the National Aeronautics and Space Administration through the NASA Astrobiology Institute under Cooperative Agreement NCC 2-1056. Work at Princeton University on this topic is supported in part by NASA grant NAG5-13148. E.B.F. acknowledges support from the Miller Institute for Basic Research.

ABBREVIATIONS

APO, Apache Point Observatory; CCD, charge-coupled device; DIS, Double Imaging Spectrograph; IR, infrared; TPF, Terrestrial Planet Finder; UV, ultraviolet.

REFERENCES

- Arcichovsky, V.M. (1912) Auf der Suche nach Chlorophyll auf den Planeten. Ann. Inst. Polytechnique Don Cesarevitch Alexis a Novotcherkassk 1(17), 195–214.
- Arnold, L., Gillet, S., Lardiere, O., Riaud, P., and Schneider, J. (2002) A test for the search for life on extrasolar planets. Looking for the terrestrial vegetation signature in Earthshine spectrum. Astron. Astrophys. 392, 231–237.
- Behrenfeld, M.J., Randerson, J.T., McClain, C.R., Feldman, G.C., Los, S.O., Tucker, C.J., Falkowski, P.G., Field, C.B., Frouin, R., Esaias, W.E., Kolber, D.D., and Pollack, N. H. (2001) Biospheric primary production during an ENSO transition. *Science* 291, 2594–2597.
- Beja, O., Spudich, E.N., Spudich, J.L., Leclerc, M., and De-Long, E.F. (2001) Proteorhodopsin phototrophy in the ocean. *Nature* 411, 786–789.
- Benedict, C.M. and Gates, D.M. (1963) Convection phenomena from planets in still air. *Am. J. Bot.* 50, 563–573.
- Butler, R.P., Marcy, G.W., Vogt, S.S., Fischer, D.A., Henry, G.W., Laughlin, G., and Wright, J.T. (2003) Seven new Keck planets orbiting G and K dwarfs. Ap. J. 582, 455–466.
- Charbonneau, D., Brown, T.M., Noyes, R.W., and Gilliland, R.L. (2002) Detection of an extrasolar planet atmosphere. *Ap. J.* 568, 377–384.
- Clark, R.N., Swayze, G.A., Gallagher, A.J., King, T.V.V., and Calvin, W.M. (1993) *The U.S. Geological Survey, Digital Spectral Library: Version 1: 0.2 to 3 Microns. U.S. Geological Survey Open File Report 93*–592, U.S. Geological Survey, Reston, VA. Available online at: http://speclab.cr.usgs.gov.

- Davis, G.R., Calcutt, S.B., Drummond, J.R., Naylor, D.A., Penny, A.J., and Seager, S. (2002) *Measurements of the Unresolved Spectrum of Earth (MUSE), Concept Study for the Canadian Space Agency*, Canadian Space Agency, University of Saskatchewan, Saskatoon.
- DeLucia, E.H., Nelson, K., Vogelmann, T.C., and Smith, W.K. (1996) Contribution of intercellular reflectance to photosynthesis in shade leaves. *Plant Cell Environ*. 19, 159–170.
- Des Marais, D.J., Harwit, M.O., Jucks, K.W., Kasting, J.F., Lin, D.N.C., Lunine, J.I., Schneider, J., Seager, S., Traub, W.A., and Woolf, N.J. (2002) Remote sensing of planetary properties and biosignatures on extrasolar terrestrial planets. *Astrobiology* 2, 153–181.
- Du, H., Fuh, R.A., Li, J., Corkan, A., and Lindsey, J.S. (1998) PhotochemCAD: A computer-aided design and research tool in photochemistry. *Photochem. Photobiol*. 68, 141–142.
- Field, B., Behrenfeld, M.J., Randerson, J.T., and Falkowski, P. (1998) Primary production of the biosphere: Integrating terrestrial and oceanic components. *Science* 281, 237–240.
- Ford, E.B., Seager, S., and Turner, E.L. (2001) Characterization of extrasolar terrestrial planets from diurnal photometric variability. *Nature* 412, 885–887.
- Frigaard, N.-U., Larsen, K.L., and Cox, R.P. (1996) Spectrochromatography of photosynthetic pigments as a fingerprinting technique for microbial phototrophs. *FEMS Microbiol. Ecol.* 20, 69–77.
- Gates, D.M., Keegan, H.J., Schleter, J.C., and Weidner, V.R. (1965) Spectral properties of plants. Appl. Opt. 4, 11–20.
- Goode, P.R., Qiu, J., Yurchyshyn, V., Hickey, J., Chu, M.-C., Kolbe, E., Brown, C.T., and Koonin, S.E. (2001) Earthshine observations of Earth's reflectance. *Geophys. Res. Lett.* 28, 1671–1674.
- Govaerts, Y.M., Jacquemoud, S., Verstraete, M.M., and Ustin, S.L. (1996) Three-dimensional radiation transfer modeling in a dicotyledon leaf. *Appl. Opt.* 35, 6585–6598.
- Grant, L. (1987) Diffuse and specular characteristics of leaf reflectance. *Remote Sensing Environ*. 22, 309–322.
- Kasting, J.F., Whitemire, D.P., and Reynolds, R.T. (1993) Habitable zones around main sequence stars. *Icarus* 101, 108–129.
- Knacke, R.F. (2003) Possibilities for the detection of microbial life on extrasolar planets. Astrobiology 3, 531–541.
- Knipling, E.B. (1970) Physical and physiological basis for the reflectance of visible and near-infrared radiation from vegetation. *Remote Sensing Environ*. 1, 155–159.
- Konrad, W., Roth-Nebelsick, A., Kerp, H., and Hass, H. (2000) Transpiration and assimilation of early Devonian land plants with axially symmetric telomes—simulations on the tissue level. *J. Theor. Biol.* 206, 91–107.
- Kuiper, G.P. (1949) *The Atmospheres of Earth and Planets*, University of Chicago Press, Chicago, p. 339.
- Lowell, P. (1911) The cartouches of the canals of Mars. *Lowell Obs. Bull.* 1(12), 59–86.
- Madigan, M.T., Martinko, J.M., and Parker, J. (2002) Brick

Biology of Microorganisms, Prentice-Hall, Upper Saddle River, NJ, p. 6.

- Mayor, M., Udry, S., Naef, D., Pepe, F., Queloz, D., Santos, N.C., and Burnet, M. (2003) The CORALIE survey for southern extra-solar planets. XII. Orbital solutions for 16 extra-solar planets discovered with CORALIE. *Astron. Astrophys.* 495, 391–402.
- McCord, Th.B., Charette, M.P., Johnson, T.V., Lebofsky, L.A., and Pieters, C. (1972) Spectrophotometry (0.3 to 1.1 micron) of visited and proposed Apollo lunar landing sites *Earth Moon Planets* 5, 52–89.
- Middleton, E. and Sullivan, J. (2000) BOREAS TE-10 Leaf Optical Properties for SSA Species. Data Set, Oak Ridge National Laboratory Distributed Active Archive Center, Oak Ridge, TN. Available on-line at: http://www.daac.ornl.gov.
- Millman, P.M. (1939) Is there vegetation on Mars? *Sky* 3, 10–11.
- Moses, J.I. and Nash, D.B. (1991) Phase transformations and the spectral reflectance of solid sulfur—can metastable sulfur allotropes exist on Io? *Icarus* 89, 277–304.
- Mulkidjanian, A.Y. and Junge, W. (1997) On the origin of photosynthesis as inferred from sequence analysis. A primordial UV-protection as common ancestor of reaction centers and antenna proteins. *Photosyn. Res.* 51, 27–42.
- Oesterhelt, D. and Stoeckenius, W. (1971) Rhopsin-like protein from the purple membrane of *Halobacterium halobium*. *Nature* 233, 149–152.
- Purves, W.K., Orians, G.H., and Heller, H.C. (1995) *Life: The Science of Biology*, Sinauer Associates, Sunderland, MA.
- Rea, D.G., O'Leary, B.T., and Sinton, W.M. (1965) Mars: The origin of the 3.58- and 3.69-micron minima in the infrared spectrum. *Science* 147, 1286–1288.
- Sagan, C. and Pollack, J.B. (1969) Windblown dust on Mars. *Nature* 223, 791–794.
- Sagan, C., Thompson, W.R., Carlson, R., Gurnett, D., and Hord, C. (1993) A search for life on Earth from the Galileo spacecraft. *Nature* 365, 715–721.

- Seager, S. (2003) The search for extrasolar Earth-like planets. *Earth Planet. Sci. Lett.* 208, 113–124.
- Seager, S. and Ford, E.B. (2004) The vegetation red edge spectroscopic feature as a surface biomarker. In Space Telescope Science Institute Symposium Series, Vol. 16: Astrophysics of Life, edited by M. Livio, I.N. Reid, and W.B. Sparks, Cambridge University Press, Cambridge, UK, pp. 67–75.
- Sinton, W.M. (1957) Spectroscopic evidence for vegetation on Mars. *Ap. J.* 126, 231–239.
- Sinton, W.M. (1958) Spectroscopic evidence of vegetation on Mars. *Publ. Astron. Soc. Pacific* 70, 50–56.
- Slaton, M.R., Hunt, E.R., and Smith, W.K. (2001) Estimating near-infrared leaf reflectance from leaf structural characteristics. *Am. J. Bot.* 88, 278–284.
- Slipher, J.M. (1924) Observations of Mars in 1924 made at the Lowell Observatory: II. Spectrum observations of Mars. *Publ. Astron. Soc. Pacific* 36, 261–262.
- Spencer, J.R. and Schneider, N.M. (1996) Io on the eve of the Galileo mission. *Annu. Rev. Earth Planet. Sci.* 24, 125–190.
- Tikhov, G.A. (1947) Etude de la lumière cendrée de la Lune au moyen des filters sélectuers. *Bull. Astron. Geodet. Soc. U.S.S.R.* 8, 15–25.
- Wolstencroft, R.D. and Raven, J.A. (2002) Photosynthesis: Likelihood of occurrence and possibility of detection on Earth-like planets. *Icarus* 157, 535–548.
- Woolf, N.J., Smith, P.S., Traub, W.A., and Jucks, K.W. (2002) The spectrum of Earthshine: A pale blue dot observed from the ground. *Ap. J.* 574, 430–433.

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