IDENTIFYING PLANETARY BIOSIGNATURE IMPOSTORS: SPECTRAL FEATURES OF CO AND O₄ RESULTING FROM ABIOTIC O₂/O₃ PRODUCTION

Edward W. Schwieterman¹,²,³, Victoria S. Meadows¹,²,³, Shawn D. Domagal-Goldman²,⁴, Drake Deming²,⁵, Giada N. Arney¹,²,³, Rodrigo Luger¹,²,³, Chester E. Harmann²,⁶,⁷,⁸, Amit Misra¹,²,³, and Rory Barnes¹,²,³

¹ Astronomy Department, University of Washington, Box 351580, Seattle, WA 98195, USA; eschwieter@uw.edu
² NASA Astrobiology Institute’s Virtual Planetary Laboratory, Seattle, WA 98119, USA
³ Astrobiology Program, University of Washington, Seattle, WA 98195, USA
⁴ NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA
⁵ Department of Astronomy, University of Maryland, College Park, MD 20742, USA
⁶ Geosciences Department, Pennsylvania State University, University Park, PA 16802, USA
⁷ Pennsylvania State Astrobiology Research Center, 2217 Earth and Engineering Sciences Building, University Park, PA 16802, USA
⁸ Center for Exoplanets and Habitable Worlds, Pennsylvania State University, University Park, PA 16802, USA

Received 2016 January 19; accepted 2016 February 16; published 2016 February 25

ABSTRACT

O₂ and O₃ have been long considered the most robust individual biosignature gases in a planetary atmosphere, yet multiple mechanisms that may produce them in the absence of life have been described. However, these abiotic planetary mechanisms modify the environment in potentially identifiable ways. Here we briefly discuss two of the most detectable spectral discriminants for abiotic O₂/O₃: CO and O₄. We produce the first explicit self-consistent simulations of these spectral discriminants as they may be seen by James Webb Space Telescope (JWST). If JWST-NIRISS and/or NIRSpec observe CO (2.35, 4.6 μm) in conjunction with CO₂ (1.6, 2.0, 4.3 μm) in the transmission spectrum of a terrestrial planet it could indicate robust CO₂ photolysis and suggest that a future detection of O₂ or O₃ might not be biogenic. Strong O₄ bands seen in transmission at 1.06 and 1.27 μm could be diagnostic of a post-runaway O₂-dominated atmosphere from massive H-escape. We find that for these false positive scenarios, CO at 2.35 μm, CO₂ at 2.0 and 4.3 μm, and O₃ at 1.27 μm are all stronger features in transmission than O₂/O₃ and could be detected with S/N ≥ 3 for an Earth-size planet orbiting a nearby M dwarf star with as few as 10 transits, assuming photon-limited noise. O₄ bands could also be sought in UV/VIS/NIR reflected light (at 0.345, 0.36, 0.38, 0.445, 0.475, 0.53, 0.57, 0.63, 1.06, and 1.27 μm) by a next generation direct-imaging telescope such as LUVOIR/HDST or HabEx and would indicate an oxygen atmosphere too massive to be biologically produced.

Key words: astrobiology – planets and satellites: atmospheres – planets and satellites: terrestrial planets – techniques: spectroscopic

1. INTRODUCTION

In recent years dozens of exoplanets have been identified that are likely or confirmed to be rocky in composition, analogous to the solar system’s inner terrestrial planets (e.g., Berta-Thompson et al. 2015). Some of these known planets reside within the habitable zone (HZ) of their host star (Kopparapu et al. 2013), but are too distant from Earth for spectroscopic follow-up to characterize their planetary environments. The upcoming Transiting Exoplanet Survey Telescope (Ricker et al. 2014; Sullivan et al. 2015) and ground-based surveys (e.g., Charbonneau et al. 2009) will identify more nearby terrestrial HZ planets that are amenable to further study by missions such as the James Webb Space Telescope (JWST; Deming et al. 2009) or large ground-based telescopes (e.g., Snellen et al. 2013). Many of these terrestrial exoplanets will have secondary atmospheres in which photochemistry, climate, history of atmospheric escape, volcanic outgassing, and perhaps biology will play significant roles in their atmospheric compositions (e.g., Segura et al. 2005, 2010). Understanding these star-planet interactions and geological processes will be important for characterizing a terrestrial planet’s atmosphere, both to understand the planetary environment, and to increase the confidence with which we can identify planetary phenomena as being more likely to be produced by life (e.g., Des Marais et al. 2002; Segura et al. 2005; Seager et al. 2012) than by abiotic processes.

Atmospheric O₂ (or its photochemical byproduct O₃) is often considered a robust astronomical biosignature, because through the history of our planet life has been the dominant source of this gas. The exact mechanism(s) and timeline for the oxygenation of Earth’s atmosphere is still under debate, but there is broad agreement on the fundamental causes (Lyons et al. 2014). The O₂ in Earth’s atmosphere is unstable over geological timescales and would be depleted by reactions with reduced volcanic gases and through oxidation of the surface (Catling 2013), thus requiring an active source to maintain appreciable levels. On Earth, that active source exists in the form of photosynthetic production of O₂ by life, followed by burial of organic carbon (Catling 2013), which separates the organic carbon material from atmospheric O₂. The photochemical production of very small amounts of O₂ occurs on Earth from the photolysis of O-bearing molecules, but would not build up to appreciable levels in the absence of biology due to the shape of the UV spectrum of the Sun and significant sinks for O₂ (Domagal-Goldman et al. 2014; Harman et al. 2015). The O₂ in Earth’s atmosphere is a result of photochemical reactions involving O₂, and the presence of large quantities of O₂ has been suggested as being an indicator of abundant, photosynthetically generated O₂ (Des Marais et al. 2002; Segura et al. 2005). Recently, it has been calculated that the strongest disequilibrium indicator in Earth’s atmosphere-ocean system in terms of free energy is the N₂–O₂–
dominated atmosphere coexisting with a liquid H2O surface ocean (Krissansen-Totton et al. 2015). The common thread to all of these signatures is the presence of photosynthetically produced O2, and there have been many studies into the feasibility of future ground-based and space-based observations to detect O2 spectral features in exoplanet atmospheres (e.g., Snellen et al. 2013; Misra et al. 2014a; Dalcanton et al. 2015).

Even though abiotic sources for abundant O2/O3 are not present for Earth, three major categories of abiotic O2 mechanisms have been recently identified that may affect planets with different atmospheric histories or within the HZs of different types of host star. These include: (1) the photochemical production of stable concentrations of O2/O3 from CO2 photolysis, which depends on the UV spectral slope of the host star and abundance of H-bearing molecules in the atmosphere (Selsis et al. 2002; Domagal-Goldman et al. 2014; Tian et al. 2014; Gao et al. 2015; Harman et al. 2015), (2) massive XUV-driven H-escape and O2-buildup on planets in the HZ during the pre-main sequence, especially for planets orbiting the latest type stars (Luger & Barnes 2015), and (3) abiotic O3 buildup due to H-escape from N2-poor atmospheres that lack tropospheric H2O cold traps (Wordsworth & Pierrehumbert 2014). In this work we refer to O2 and O3 produced by these abiotic processes as biosignature impostors.

Understanding potential false positives for O2/O3 biosignatures is critical and timely for informing the search for life beyond the solar system, given that the first potentially habitable planets to be characterized with transmission observations will likely orbit M dwarfs, and so will be most susceptible to O2 biosignature impostors through CO2 photolysis and XUV-driven hydrogen escape (mechanisms (1) and (2) above).

Possible discriminants for false positive mechanisms have previously been discussed in the literature. For instance, identifying the byproducts of CO2 photolysis using direct imaging was discussed in recent papers that described this false positive mechanism (Domagal-Goldman et al. 2014; Harman et al. 2015). N2-depleted atmospheres without a cold trap (mechanism (3)) may be identified via the absence of pressure-sensitive N2–N2 collisionally induced absorption (CIA) features (Schwieterman et al. 2015). However, previous studies have not addressed identification of CO2 photolysis with transmission spectroscopy, or identification of the O2-dominated atmospheres that result from massive H-escape. The O2 abundance on Earth has self-limited to $\lesssim$0.3 bar due to the chemical instability of higher O2 abundances with organic matter (Kump 2008). Thus, the potentially very high O2 pressures from massive H-loss would constitute a separate and discernable regime from biologically produced O2 atmospheres.

Here we examine the detectability, in simulated JWST transmission spectra, of CO from CO2 photolysis as an indicator for abiotically generated O2/O3 for a terrestrial HZ planet orbiting an M dwarf. We also examine the detectability of highly pressure-dependent O2–O2 (O2) CIA features in transmission and reflectance spectroscopy. These features would be indicators of massive, post-runaway, abiotic O2 atmospheres. This examination builds on earlier work by (Misra et al. 2014a) that analyzed the capacity of O2 bands to determine pressure in O2-rich atmospheres, which were presumed to be photosynthetically generated. In Section 2, we describe the models used and the inputs to those models.

Section 3 we present the spectra of the biosignature impostor scenarios and the detectability of our proposed spectral discriminators. We discuss some of the implications of these results in Section 4 and present our conclusions in Section 5.

2. METHODS AND MODELS

2.1. Atmosphere Profiles

2.1.1. High-CO Photochemical False Positive

The first atmosphere scenario we consider is a habitable, but lifeless, planet with an N2–CO2–H2O atmosphere, orbiting in the HZ of a late (M or K) type dwarf and susceptible to the abiotic accumulation of O2 and CO through CO2 photolysis:

$$\text{CO}_2 + h\nu (\lambda < 175 \text{ nm}) \rightarrow \text{CO} + \text{O}. \quad (1)$$

Photochemically liberated O will lead to the formation of both O2 and O3 through the Chapman scheme, reviewed in Domagal-Goldman et al. 2014. For this scenario we use the high-O2 case for GJ 876 from Harman et al. 2015 (as our atmospheric chemical and temperature profiles (Figure 1(a)), as that case led to potentially detectable levels of O2. GJ 876 is a planet-hosting M4V star with $R_*=0.38 \, R_\odot$, located 4.66 pc from the solar system (von Braun et al. 2014). The modeled planet orbits at a semimajor axis of 0.15 au. Its N2-dominated atmosphere contains 5% CO2, 6% O2 and 2% CO. The temperature profile was calculated in Harman et al. 2015 by assuming a surface temperature commensurate with the stellar insolation and a moist adiabatic lapse rate to an isothermal stratosphere of 175 K. The isothermal stratosphere produces a conservative estimate of the scale height (and therefore transit depths) by neglecting shortwave heating of O3. Isothermal stratospheres are commonly chosen in studies of abiotic O2 generation (e.g., Domagal-Goldman et al. 2014; Tian et al. 2014) and we adopt this assumption here to be consistent with previous literature.

2.1.2. O2-dominated Post-runaway Atmospheres

Luger & Barnes 2015 calculate that up to thousands of bars of abiotic O2 can be generated by XUV-driven H-escape during the pre-main sequence phase of the planet’s host star. This
depends on a number of factors, including the starting H₂O inventory (losing the H from one Earth ocean leaves behind up to 240 bar of O₂). Some of this O₂ would oxidize the surface; however we assume that there is a point where the oxidation of the planetary surface is complete and O₂ remains stable in the atmosphere. Even if geological processes slowly draw down this remaining O₂, much could remain for extended time periods, limited by the rate of mantle overturn. Since many parameters determine how much (if any) abiotic O₂ would remain behind on these planets when they are observed, we therefore prescribe a range of surface pressures with a 95% O₂ mixing ratio: \( P_0 = 1, 10, \) and 100 bar. The CO₂ content is similar to Earth’s, \( f_{CO_2} = 3.6 \times 10^{-4} \), and the rest of the atmosphere consists of N₂ and trace photochemically produced species such as CO and O₃. To self-consistently calculate temperature and ozone profiles, we used a version of the coupled photochemical-climate model Atmos (Arney et al. 2016), based on photochemical and climate models originating with the Kasting group (Kasting & Donahue 1980; Segura et al. 2005; Haqq-Misra et al. 2008; Domagal-Goldman et al. 2014) and upgraded to handle high-pressure O₂-dominated atmospheres. We assume a completely desiccated planet (no H₂O) orbiting at the inner edge of the HZ \((a = 0.12 \text{ au})\) of a star with identical properties to GJ 876. See Figure 1(b) for the atmospheric chemical profiles of the \( P_0 = 100 \) bar scenario.

2.2. Radiative Transfer Models and Inputs

The core radiative transfer code used for this work is the Spectral Mapping Atmospheric Radiative Transfer (SMART) model developed by D. Crisp (Meadows & Crisp 1996; Crisp 1997), which is a line-by-line, multi-stream, multi-scattering model. SMART is well-validated from data-model comparisons of Earth, Venus, and Mars (e.g., Robinson et al. 2011, 2014; Arney et al. 2014). SMART can be used to calculate synthetic direct-imaging spectra and transmission spectra using a transmission capable version of SMART that includes refraction (Misra et al. 2014a, 2014b). All modeled spectra include O₃ absorption \((O_2–O_2\text{ CIA})\), although it only produces a strong spectral impact in the cases with O₂-dominated atmospheres. Weak O₂ bands are present in Earth’s disk-averaged spectrum (Tinetti et al. 2006; Turnbull et al. 2006). O₂ absorption has been found to be only very weakly temperature-dependent, suggesting that O₂–O₂ CIA dominates over true van der Waals molecule absorption (Thalman & Volkamer 2013). The CIA absorption from O₃ varies quadratically with density, and the absorption coefficients can be given as:

\[
\alpha(\lambda, T, d_{O_3}) = B_{O_2–O_2}(\lambda, T) d_{O_3}^2 \approx B_{O_2–O_2}(\lambda) d_{O_2}^2 \tag{2}
\]

where \(\alpha\) is the absorption coefficient, \(d_{O_3}\) is the density of O₃ molecules, and \(B_{O_2–O_2}\) is a density-normalized CIA coefficient. We use the density-normalized O₃ coefficients from C. Hermans\(^1\) for the 0.333–0.666 \(\mu\)m spectral range (Hermans et al. 1999), and the values from Greenblatt et al. (1990) and Maté et al. (1999) for the 1.06 and 1.27 \(\mu\)m features.

2.3. JWST NIRISS and NIRSpec Noise Model

We calculated the synthetic JWST observations as described by Deming et al. (2009) with some updates. The total throughput of the NIRISS (Doyon et al. 2014) and NIRSpec (Ferruit et al. 2014) instruments, including the telescope, were taken from L. Albert (2015, private communication) and from http://www.cosmos.esa.int/web/jwst/nirspec-pce, respectively. Thermal and zodiacal background were included as described by Deming et al. (2009), but the background only becomes significant longward of approximately 4 \(\mu\)m. There is very little overhead for NIRISS transit spectroscopy (L. Albert 2015, private communication), so we adopted an observing efficiency of unity for NIRISS. For NIRSpec, we calculated the observing efficiency assuming a 2048 × 32 subarray (Tumlinson 2010), and adopted a number of groups in an integration (ngp) of 4 from Karakla et al. (2010). For both instruments, the observations are close to saturation, but we assume that saturation can be avoided by slightly dithering or scanning the telescope perpendicular to dispersion. We adopt photon-limited noise, dropping the hypothetical instrument systematic noise used by Deming et al. (2009). Recent Hubble Space Telescope experience has demonstrated close to photon-limited performance for bright stars (Kreidberg et al. 2014). We represent the star using a Phoenix model atmosphere (Allard & Hauschildt 1995).

3. SIMULATED SPECTRA OF ATMOSPHERES WITH ABIOTIC O₂

We present photochemically self-consistent test cases for two different false positive mechanisms: (1) an Earth-size planet with a prebiotic atmosphere (Figure 1(a)) orbiting in the HZ of GJ 876, and (2) an Earth-size planet with an O₂-dominated (95%) 100 bar atmosphere orbiting at the inner edge of the HZ of GJ 876 (Figure 1(b)). These atmospheres are free of clouds and aerosols. We examine scenario (2) in transmitted and reflected light. In the reflected light case we treat GJ 876 as a stand-in for the handful of nearby late-type stars whose HZs may be examined with future direct-imaging telescopes such as HDST/LUVOIR (Stark et al. 2014; Dal Canton et al. 2015).

Figure 2 shows the calculated spectral transmission depths and simulated observations of case (1) in the JWST NIRISS (0.6–2.5 \(\mu\)m) and NIRSpec (2.9–5.0 \(\mu\)m) bands (left panel). Our calculations show that the 1.65, 2.0, and 4.3 \(\mu\)m CO₂ bands can be detected with an S/N > 3 (3.1, 4.3 and 8.0, respectively) when binned across the absorption bands and compared to the continuum level. The 2.35 \(\mu\)m CO band has an S/N of 3.7 while the 4.6 \(\mu\)m CO band has an S/N of 2.6. Other absorption bands have \(S/N < 1\). The simultaneous detection of both CO₂ and CO could indicate CO₂ photolysis in the planet’s atmosphere. Note that for the integration time used here, the relatively narrow O₂–A band (0.76 \(\mu\)m) and weaker O₂ features would not be detectable. On the right side panel of Figure 2 we show a spectrum of modern Earth orbiting GJ 876 using atmosphere profiles from Figure 1 of Schwieterman et al. (2015), but with otherwise the same parameters as the left panel. This spectrum is not self-consistent with the star, but provided for comparison.

Figure 3 shows the calculated transmission spectrum depths of the high-O₂ atmosphere from case (2). The S/Ns of the 1.06 and 1.27 \(\mu\)m O₂ bands are 2.8 and 3.1, respectively. The detection of strong O₂ bands would indicate a very massive O₂ atmosphere free of aerosols at high altitudes.

In Figure 4, we show simulated reflectance (direct-imaging) spectra of O₂-dominated atmospheres (\(P_0 = 1, 10, \) and 100 bar) seen at quadrature (solar zenith angle of 60°) using

\(^{10}\) http://spectrolab.aeronomie.be/o2.htm
SMART. We use the chemical profiles described in Section 2.1.2. For comparison we include the spectrum of an Earth atmosphere (Schwieterman et al. 2015). A gray surface albedo of $A_g = 0.15$ is assumed. The O$_4$ bands at 0.345, 0.36, 0.38, 0.445, 0.475, 0.53, 0.57, 0.63, 1.06, and 1.27 μm are labeled, with the NIR bands saturating at the highest O$_2$ abundance. This simple test case demonstrates that if the high-O$_2$ atmospheres proposed by Luger & Barnes (2015) exist, the O$_4$ absorption band strength in those planetary spectra would rival or exceed that of the monomer O$_2$ bands. These spectra are qualitatively different than modern-Earth’s spectrum, even in the 0.3–1.0 μm range, with a different shape, broader O$_2$ features, and additional features from O$_4$. These are all signs of a much higher O$_2$ abundance than the Earth’s atmosphere—self-regulated by negative feedbacks—has ever achieved.

4. O$_4$ AND CO AS SPECTRAL INDICATORS OF ABIOTIC OXYGEN

The first potentially habitable terrestrial planet atmospheres to be characterized via transmission spectroscopy by JWST or large ground-based observatories will likely be orbiting near the inner edge of the HZ of late type stars (Deming et al. 2009; Sullivan et al. 2015). This is due to the detection biases of planet transit searches and the shorter orbital periods of HZ planets around late type stars, allowing greater potential to integrate over multiple transits for characterization. Unfortunately, according to current modeling studies (Harman et al. 2015; Luger & Barnes 2015) these planets are the worlds in which biosignature impostors—abiotic O$_2$ and O$_3$—are most likely. Furthermore, this potential for false positives for life is even greater for the extended inner HZ for dry planets (Abe et al. 2011), which may have an even greater probability of being characterized first. The development of observing strategies to mitigate the potential for a false positive biosignature detection is thus relevant now. We argue that the detection of significant CO and CO$_2$ could indicate robust CO$_2$ photolysis, which can produce abiotic O$_2$/O$_3$, and also that strong O$_4$ bands would be indicative of an oxygen atmosphere too massive to be biological. Thus CO$_2$/CO and O$_4$ are potentially powerful spectral discriminators against abiotic O$_2$/O$_3$ in future potentially habitable exoplanet observations.

Figure 2. Left: spectrum (blue) of photochemical high-O$_2$/CO GJ 876 atmosphere from Harman et al. (2015) in the JWST-NIRISS band (top) and in the JWST-NIRspec band (bottom). Data points and 1σ error bars were generated with the JWST instrument simulator (Deming et al. 2009) assuming 65 hr integrations (10 transits of GJ 876) and photon-limited noise. Right: comparable model spectrum (green) of Earth orbiting GJ 876 using atmosphere profiles taken from Figure 1 of Schwieterman et al. (2015).
Furthermore, in the cases presented here, the spectral discriminators against abiogenic O2/O3 are more detectable with a hypothetical JWST observation than the O2 or O3 signatures themselves. In our example spectra, neither O2 nor O3 would be directly detectable with just 10 transits, but the abiogenic discriminators CO/O2 and O4 could be. This provides an opportunity to maximize the utility of observing time if the ultimate goal is to characterize planets where true biosignatures are obtainable. If spectral indicators for biosignature impostors are detected with reasonable confidence, the community may wish to reallocate the remaining time to other promising targets, rather than integrate further. Additionally, it may also be the case that O2 or O3 may be identified in the same targets via other observing strategies at a concurrent or future date. For example, it has been proposed that O2 may be found via ground-based Extremely Large Telescope (ELT) observations of the 0.76 µm O2-A (Snellen et al. 2013). Observations by space-based telescopes such as JWST or a future LUVOIR telescope operating in transit mode on a favorable target could detect or rule out these indicators before significant observing time is expended by ELTs on promising targets. If an ELT observation of a potentially habitable planet is conducted, these potential spectral discriminators could be characterized in addition to the target band (e.g., the O2-A band).

It is important to note that the strength of an absorption band in transmission, unlike in reflected light, is not dependent on the mixing ratio of the gas at the surface or the absolute column abundance of the gas. Rather, the strength is mostly dependent on the altitude at which the gas produces an optical depth near unity, and thus the distribution of the gas in the atmosphere is extremely important. Direct imaging of CO2 and CO spectral signatures on an Earth twin is potentially problematic because they are weak and narrow shortward of 2.0 µm and the planetary flux at the strongest bands (e.g., the 4.3 µm CO2 band) is low (Robinson et al. 2014; Schwieterman et al. 2015). Our work shows these bands are much stronger in transmission. Thus transmission spectroscopy is complementary to potential future direct-imaging characterization missions, and in particular for characterizing potential biosignature impostors. Transmission spectroscopy is also more sensitive to Earth-like CH4 abundances than direct-imaging. Detection of CH4 with O2/O3 would help confirm a true biosignature, as modeling predicts extremely low CH4 abundances in cases of abiogenic O2/O3 generation (Domagal-Goldman et al. 2014).

Next-generation space-based direct-imaging telescope concepts such as ATLAST/LUVOIR, HDST, and HabEx would be able to directly image planets in the HZ (Dalcanton et al. 2015; Rauscher et al. 2015; Swain et al. 2015), and thus potentially characterize biosignature gases in exoplanet atmospheres. Detection of strong O4 bands in UV/VIS/NIR reflected light would indicate a large O2 atmosphere originating from massive H-escape. While planets in the conservative HZ of G and F type stars would be high priority for these missions and are less susceptible to an extended history of runaway H-loss and O2-buildup, planets orbiting between the optimistic (recent Venus) and conservative (runaway greenhouse) inner edge of the HZ, potentially brighter targets for imaging, would also be susceptible to this process (Luger & Barnes 2015). Additionally, many nearby K and M type stars would also likely be characterized (Stark et al. 2014; Dalcanton et al. 2015), where larger regions of the HZ would be susceptible to generating biosignature impostors.
5. CONCLUSIONS

Recently proposed mechanisms for developing abiotic O$_2$/O$_3$ in terrestrial exoplanet atmospheres would produce spectral discriminators that are potentially identifiable with future telescope observations, including JWST. These discriminators are more detectable than O$_2$ or O$_3$ in transmission observations. CO seen at 2.35 μm or 4.6 μm with CO$_2$ at 2 or 4.3 μm would indicate robust CO$_2$ photolysis and suggest a high likelihood of abiotic O$_2$/O$_3$ generation. We find that CO in a realistic exoplanet atmosphere orbiting a late type star could be seen with an S/N > 3 at 2.35 μm in JWST-NIRISS with as few as 10 transits. O$_4$ bands seen in transmission or direct-imaging can be diagnostic of high-O$_2$ post-runaway atmospheres that have experienced a history of H-escape. The 1.06 and 1.27 μm O$_4$ bands in a massive, O$_2$-dominated atmosphere without high-altitude aerosols would be potentially detectable with an S/N > 3 with as few as 10 transits with JWST-NIRISS, assuming photon-limited noise.

This work was supported by the NASA Astrobiology Institute’s Virtual Planetary Laboratory Lead Team, funded through the NASA Astrobiology Institute under solicitation NNH12ZDA002C and Cooperative Agreement Number NNA13AA93A. This research used the advanced computational, storage, and networking infrastructure provided by the Hyak supercomputer system at the University of Washington. This work made use of the NASA Astrophysics Data System. We would like to thank the anonymous reviewer for helpful comments, which improved the manuscript.

REFERENCES

Abe, Y., Abe-Ouchi, A., Sleep, N. H., & Zahnle, K. J. 2011, AsBio, 11, 443
Allard, F., & Hauschildt, P. H. 1995, ApJ, 445, 433
Arney, G., Domagal-Goldman, S. D., Meadows, V. S., et al. 2016, AsBio, submitted
Arney, G., Meadows, V., Crisp, D., et al. 2014, JGRE, 119, 1860
Berta-Thompson, Z. K., Irwin, J., Charbonneau, D., et al. 2015, Natur, 527, 204
Cating, D. C. 2013, Treatise on Geochemistry, Vol. 6 (2nd ed.; Amsterdam: Elsevier), 177
Charbonneau, D., Berta, Z. K., Irwin, J., et al. 2009, Natur, 462, 891
Crisp, D. 1997, GeoRL, 24, 571
Dalcanton, J., Seager, S., Aigrain, S., et al. 2015, arXiv:1507.04779
Deming, D., Seager, S., Winn, J., et al. 2009, PASP, 121, 952
Des Marais, D. J., Harwit, M. O., Jucks, K. W., et al. 2002, AsBio, 2, 153
Domagal-Goldman, S. D., Segura, A., Claire, M. W., Robinson, T. D., & Meadows, V. S. 2014, ApJ, 792, 90
Doyon, R., Lafrenière, D., Albert, L., et al. 2014, in Search for Life Beyond the Solar System Exoplanets, Biosignatures and Instruments, ed. D. Apai, & P. Gabor (Tucson, AZ), 3.6
Ferruit, P., Birkmann, S., Boker, T., et al. 2014, Proc. SPIE, 9143, 91430A
Gao, P., Hu, R., Robinson, T. D., Li, C., & Yung, Y. L. 2015, ApJ, 806, 249
Greenblatt, G. D., Orlando, J. J., Burkholder, J. B., & Ravishankara, A. R. 1990, JGR, 95, 18577
Haqq-Misra, J. D., Domagal-Goldman, S. D., Kasting, P. J., & Kasting, J. F. 2008, AsBio, 8, 1127
Harman, C. E., Schwieterman, E. W., Schottelkotte, J. C., & Kasting, J. F. 2015, ApJ, 812, 137
Hermans, C., Vandaele, A. C., Carleer, M., et al. 1999, Environ. Sci. Pollut. Res., 6, 151
Karakla, D., Beck, T., Blair, W., et al. 2010, Document JWST-STScI-002129, SM-12 (Baltimore, MD: STScI)
Kasting, J. F., & Donahue, T. M. 1980, JGR, 85, 3255
Kopparapu, R. K., Ramirez, R., Kasting, J. F., et al. 2013, ApJ, 765, 131
Kreidberg, L., Bean, J. L., Désert, J.-M., et al. 2014, Natur, 505, 69
Krisssansen-Totton, J., Bergsmann, D. S., & Catling, D. C. 2015, AsBio, 16, 39
Kump, L. R. 2008, Natur, 451, 277
Luger, R., & Barnes, R. 2015, AsBio, 15, 119
Mahony, J. S., & Kasting, J. F. 2016, ApJ, 812, 137
Meadows, V. S. 2014, ApJ, 792, 61
Meadows, V., & Crisp, D. 1996, JGR, 101, 4595
Misra, A., Meadows, V., & Crisp, D. 2014a, AsBio, 14, 67
Misra, A., Meadows, V., & Crisp, D. 2014b, ApJ, 792, 61
Rauscher, B. J., Bolcar, M. R., Clampin, M., et al. 2015, Proc. SPIE, 9602, 9602D
Ricker, G. R., Winn, J. N., Vandersteek, R., et al. 2014, Proc. SPIE, 9413, 941320
Robinson, T. D., Ennico, K., Meadows, V. S., et al. 2014, ApJ, 787, 171
Robinson, T. D., Meadows, V. S., Crisp, D., et al. 2011, AsBio, 11, 393
Schwieterman, E. W., Robinson, T. D., Meadows, V. S., Misra, A., & Domagal-Goldman, S. 2015, ApJ, 810, 57
Seager, S., Schrenk, M., & Bains, W. 2012, AsBio, 12, 61
Segura, A., Kasting, J. F., Meadows, V., et al. 2005, AsBio, 5, 706
Selsis, F., Despois, D., & Pariset, J.-P. 2002, A&A, 388, 985
Snellen, I. A. G., de Kok, R. J., Le Poole, R., Brogi, M., & Birkby, J. 2013, ApJ, 764, 182
Stark, C. C., Roberge, A., Mandell, A., & Robinson, T. D. 2014, ApJ, 795, 122
Sullivan, P. W., Winn, J. N., Berta-Thompson, Z. K., et al. 2015, ApJ, 809, 77
Swain, M. R., Greenblatt, G. D., Clampin, M., et al. 2009, HabEx science at modest cost, http://cor.gsfc.nasa.gov/copag/rf/HabEx_2020_30apr2015_submitted.pdf
Thalmann, R., & Volkamer, R. 2013, PCCP, 15, 15371
Tian, F., France, K., Linsky, J. L., Mauas, P. J. D., & Vicyes, M. C. 2014, E&PSL, 385, 22
Tinetti, G., Meadows, V. S., Crisp, D., et al. 2006, AsBio, 6, 34
Tumlinson, J. 2010, Document JWST-STScI-002129, SM-12
Turnbull, M. C., Traub, W. A., Jucks, K. W., et al. 2006, ApJ, 644, 551