

Atmospheric carbon depletion as a tracer of water oceans and biomass on temperate terrestrial exoplanets

Amaury Triaud, Julien de Wit, Frieder Klein, Benjamin Rackham, Martin Turbet, Prajwal Niraula, Ana Glidden, Oliver Jagoutz, Matej Peč, Janusz Petkowski, et al.

▶ To cite this version:

Amaury Triaud, Julien de Wit, Frieder Klein, Benjamin Rackham, Martin Turbet, et al.. Atmospheric carbon depletion as a tracer of water oceans and biomass on temperate terrestrial exoplanets. Nature Astronomy, 2024, 8 (1), pp.17-29. 10.1038/s41550-023-02157-9. hal-04790253

HAL Id: hal-04790253 https://hal.science/hal-04790253v1

Submitted on 19 Nov 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Atmospheric carbon depletion as a tracer of water oceans and biomass on temperate terrestrial exoplanets

Amaury H.M.J. Triaud^{1,+,*}, Julien de Wit^{2,+,*}, Frieder Klein³, Martin Turbet⁴, Benjamin V. Rackham^{2,5}, Prajwal Niraula², Ana Glidden^{2,5}, Oliver E. Jagoutz², Matej Peč², Janusz J. Petkowski^{2,6,7}, Sara Seager^{2,8,9}, Franck Selsis¹⁰

⁺These authors contributed equally to this work.

¹School of Physics and Astronomy, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom;

²Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, USA;

³Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA;

⁴Laboratoire de Météorologie Dynamique/IPSL, CNRS, Sorbonne Université, École Normale Supérieure, PSL Research University, École Polytechnique, 75005 Paris, France;

⁵Kavli Institute for Astrophysics and Space Research, Massachusetts Institute of Technology, Cambridge, MA 02139, USA;

⁶JJ Scientific, 02-792 Warsaw, Poland;

⁷Faculty of Environmental Engineering, Wroclaw University of Science and Technology, 50-

^{*}corresponding authors (a.triaud@bham.ac.uk and jdewit@mit.edu)

370 Wroclaw, Poland;

⁸Department of Physics, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA;

⁹Department of Aeronautics and Astronautics, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA

¹⁰Laboratoire d'astrophysique de Bordeaux, Univ. Bordeaux, CNRS, B18N, allée Geoffroy Saint-Hilaire, 33615 Pessac, France.

The conventional observables to identify a habitable or inhabited environment in exoplanets, such as an ocean glint or abundant atmospheric O_2 , will be challenging to detect with present or upcoming observatories. Here we suggest a new signature. A low carbon abundance in the atmosphere of a temperate rocky planet, relative to other planets of the same system, traces the presence of substantial amount of liquid water, plate tectonic and/or biomass. We show that JWST can already perform such a search in some selected systems like TRAPPIST-1 via the CO_2 band at $4.3\,\mu\text{m}$, which falls in a spectral sweet spot where the overall noise budget and the effect of cloud/hazes are optimal. We propose a 3-step strategy for transiting exoplanets: 1) detection of an atmosphere around temperate terrestrial planets in ~ 10 transits for the most favorable systems, (2) assessment of atmospheric carbon depletion in ~ 40 transits, (3) measurements of O_3 abundance to disentangle between a water- vs biomass-supported carbon depletion in ~ 100 transits. The concept of carbon depletion as a signature for habitability is also applicable for next-generation

direct imaging telescopes.

1 The challenge of detecting exohabitats this decade

In 2022, humanity entered a new era of space exploration when the very first data products from the James Webb Space Telescope (JWST) were revealed ^{1–5}. JWST is the first of a new generation of great observatories to come online this decade and scientific accomplishments such as probing the atmospheres of terrestrial exoplanets and 3D-mapping of giant exoplanets are now within reach.

The greatest potential for exoplanetary science lies in the detailed atmospheric characterization of a diverse range of planets to enable comparative studies informing formation, evolution, and atmospheric processes, as well as investigating and contextualizing habitats ⁶. Thus, our community must find and then reliably study planets suited for such quests. Over the last two decades, space- and ground-based facilities have successfully delivered on this first task, yielding over 5,200 exoplanets and close to 10,000 planetary candidates (see the NASA Exoplanet Archive). With the Extremely Large Telescopes (ELTs) and JWST coming online this decade, the field of exoplanetary science is transitioning from an era of detection into one of characterization.

Observational methods developed and refined over the past two decades now allow astronomers to collect a vast host of information about an exoplanet's atmosphere without having to leave the Solar System ⁷. When a planet transits in front of its host star, it is possible to derive constraints on the vertical temperature, pressure, and compositional profile of atmospheric limbs ^{8–12}. This provides information about the materials used during planetary assembly and their subsequent orbital evolution ^{13,14}, while also revealing the current thermodynamic state of the planet ¹⁵. High-resolution spectra can distinguish molecules with different isotopes ^{16,17}, measure wind velocities ^{18,19}, and probe evaporating exospheres ^{20,21}. There are also methods to create crude topological and atmospheric maps for exoplanets ^{22–26}.

Widely applied to hot close-in gas giants ^{27,28}, these methods are now increasingly in development and will soon be applied to terrestrial planets ^{29–33}, initiating the exploration of how diverse the atmospheric and climatic properties of exoplanets are ³⁴ and, importantly, how those compare to the properties of planets within our Solar System. Several teams have modeled terrestrial planet atmospheres ^{35–38}, while others have assessed their observability ^{39–45}. Thanks to JWST and the ELTs, the time has come to move from theoretical considerations to empirical verification and exploration.

These studies find the atmospheres of transiting temperate (defined as receiving a flux between $4\times$ and $0.25\times$ that of the Earth) terrestrial planets orbiting nearby ultra-cool dwarfs like TRAPPIST-1 ⁴⁶ can be detected with JWST and their dominant atmospheric absorbers (e.g., CO_2 and H_2O) revealed with after collecting of the order of ten transits ^{41,47}. In addition, they show that the conventional biosignature gas O_2 ^{48,49} remains out of reach with JWST due to the

narrowness of the O_2 lines combined with a low signal-to-noise ratio below 1 μm even for ideal terrestrial planet targets (i.e., those orbiting late M dwarfs, because of the much reduced size of their host star and the shortness of their temperate orbits ^{50,51}). "Biosignatures" are defined as observables associated with the presence of life. Even the anti-biosignature O₂- X collisionally induced absorption (CIA) band at 6.4 μ m, which is more readily accessible, remains mostly out of reach 43 . Indeed, detecting O_2 would require on the order of one thousand planetary transits for the most favorable targets, which corresponds to the allowable observation time over an entire JWST cycle. It would take a few decades to collect data for planets that have orbital periods of 5 to 10 days, such as those within the habitable zone of TRAPPIST-1. In other words, with this new generation of great observatories and programs gathering up to a few hundred planetary transits of terrestrial worlds, it will be possible to reveal atmospheric constituents that are strong absorbers and later derive preliminary constraints on abundances and temperature-pressure profiles, but these observations are not expected to assess the presence of life via O₂ detection. The detection of O₂ using the ELTs appears much more promising by co-adding the individually-resolved lines of its visible and near-infrared bands (e.g., the 760nm A-band) which takes advantage of high-resolution spectrographs 52-54. The detection of O₂ 55 will be attempted using transit spectroscopy (which might be difficult, 56), but also with reflected light spectroscopy (using the High-Resolution High-Contrast technique ^{57,58}) which is available for a couple of nearby non-transiting exoplanets (e.g., Proxima b) ^{58,59}. Another biosignature of interest is O_3 , produced when a large reservoir of O_2 is UV irradiated ^{48,49}. O_3 bands in the UV and optical are usually sought after for Earth-twins orbiting Solar twins, but for late-M-dwarf hosts, faint in the optical and UV, O_3 's $4.8~\mu m$ band is the most prominent feature, and of interest to this paper.

Similarly, the assessment of a planet's habitability (defined as a planet's capacity to retain large reservoirs of surface liquid water ⁶⁰) is difficult. A planet's habitability can be affected by a large range of factors, including its orbital properties, its bulk properties, the presence or lack of plate tectonics and magnetic fields, its atmospheric properties, and finally by stellar activity ⁶¹presenting a complex, and thus far a mostly theoretical assessment. Empirical measurements affected by the presence of surface liquid water would be handy; however, very few such observables of habitability ("habsignatures", defined in a similar way to "biosignature" but applied to signatures of surface liquid water) exist. Examples include detecting an ocean glint ⁶², as has been done for Titan ⁶³, but which is expected to be extremely challenging for exoplanets ⁶⁴. The presence of surface liquid water oceans could also produce a significant hydrogen exosphere, detectable in Ly α 65,66. However, this is a challenging habsignature too as it would not directly point to water as the related hydrogen-bearing molecule, nor whether water is present in its liquid phase ⁶⁷ and is a method limited to the very nearest planetary systems due to interstellar absorption. The closest yet to a habsignature is the measure of atmospheric SO2, a molecule that quickly dissolves in liquid water. Its presence in large quantities in an exoplanet's atmosphere would indicate the absence of large bodies of liquid water ^{68,69}. Because of the relation between the carbon cycle on Earth and its tectonic activity, we note that a "habsignature" might also indicate the presence of plate tectonics on exoplanets.

In this context, we propose that observations of CO_2 absorption in exoplanetary spectra can be used as a signature for habitability (since CO_2 can be removed from the atmosphere by dissolving into surface liquid water before being stored within the crust by tectonic activity) and also potentially as a biosignature (since biology traps carbon, for instance, as sediments and hydrocarbon deposits). The use of CO_2 depletion ("d CO_2 ") as a habsignature provides a rapid empirical diagnostic about which terrestrial exoplanets are likely to be habitable (i.e. host surface liquid water). This approach also happens to identify planets that are most similar to the current Earth. The main concepts of this paper are represented schematically in Figure 1.

2 Reframing the search for liquid water and signs of life

Conventionally, the search for liquid water and for signs of biology rely on the detection of added observables to the planetary signal. Ocean glints ⁶² and hydrogen exospheres ⁶⁵ are both added signals to the planet's. For life, observables are limited to atmospheric compounds viewed as "life products" that otherwise would not be thermodynamically stable within the atmosphere of a lifeless planet. Examples shown in Figure 2 include the presence of a high concentration of O₂, which itself can yield O₃ ^{48,49} and ionospheric O⁺ ⁷⁰, the presence of CH₄ within a CO₂-dominated atmosphere ⁷¹, and the presence of other hydrocarbons (e.g., ethane ⁷², chlorofluorocarbons ⁴⁴, etc.) or other molecules (e.g., nitrogen compounds ^{73,74}). Here, we propose to reframe this search by detecting the depletion of an observable rather than the addition of one. By doing so, we provide a new framework to consider the search for signs

of liquid water and/or life which will result in new pathways for these quests, complementary to those presented previously in the literature, thereby improving the prospects of identifying habitable/inhabited worlds. We present one such new pathway below.

One of the most striking differences between present-day Earth and its neighboring planets relates to its low atmospheric carbon mixing ratio. As shown in Figure 2, Earth's atmosphere has a remarkably low level of carbon dioxide among Solar System terrestrial planets. While the atmospheres of Venus and Mars are composed of >95% CO₂, Earth's atmosphere only contains $\sim 0.04\%$ CO₂ ⁷⁵. Most of the atmospheric CO₂ that was present on early Earth is now sequestered in its rocks ^{76–78}. Within an order of magnitude, there is a similar mass of carbon nowadays within Venus's atmosphere as there is locked as minerals within Earth's crust ^{76,79}. Earth's atmospheric carbon has been depleted by its hydrosphere and its biosphere. This is why atmospheric carbon depletion in a temperate rocky planet is a tracer of water oceans (a habsignature), or biomass (a biosignature), or both at once, which we refer to as a "habiosignature" (Figure 2). Transition periods such as the Archean, during which Earth was both habitable and inhabited, might be harder to diagnose with dCO₂. However, we note that Earth's atmosphere, whilst possessing a much larger carbon content than current day's, already had a depleted CO₂ level (ranging from $\sim 10\%$ at 4 Gyr to $\sim 2\%$ at 2.5 Gyr), with N₂ already being the dominant compound 80.

Atmospheric carbon depletion as a biosignature Biology -as we know it- does not just produce chemicals, it also consumes them. Thus, biology cycles elements and removes some molecules from its environment, such as sulfur, nitrogen, and carbon-bearing molecules to make other products 81. Here, we focus on carbon cycling and more specifically, on the removal of atmospheric CO₂, which is expected to be the primary carbon-bearing molecule in the atmosphere of terrestrial planets 82. The two main processes for biological carbon-dioxide depletion on Earth are (1) oxygenic photosynthesis, where carbon is sequestered in soils and hydrocarbon deposits, and (2) the creation of shells, made from calcite and aragonite (CaCO₃), which are stored as sediments in rivers and oceans ^{83,84}. Accordingly, life on Earth plays a substantial role in the carbon cycle 85 with about 20% of modern global carbon sequestration being biologicallydriven ⁸⁶. In fact, biology's ability to extract carbon from the atmosphere may have initiated one of the *snowball Earth* events ⁸⁷. This being written, in most cases it is expected that biology plays a minor role in the sequestration of carbon, as its ability to fix carbon is ultimately capped by the water cycle within which it operates 86. Therefore, other signatures, such as O₃, need to be considered to fully ascertain the presence of biological activity when a substantial depletion of atmospheric carbon is detected. We address this point in Section 3.

Similar arguments have been proposed to interpret a depletion of SO₂ ^{88,89} in the clouds of Venus, low concentrations of hydrogen compounds on Titan ^{90,91}, and depleted CO within methane-rich atmospheres ^{92–95}. Although controversial, a related example to a depletion as a signature in exoplanet literature is the concept of anti-biosignatures (e.g. large concentration of

CO 96,97 or H_2 49,98), where in that particular context the absence of a depletion is proposed as the signal.

Atmospheric carbon depletion as a habsignature Liquid water readily dissolves atmospheric CO₂ ^{99,100} which can facilitate the formation of carbonates ¹⁰¹, creating a detectable habsignature ¹⁰². CO₂ is expected to dominate the speciation of outgassing products of rocky planets with a bulk composition and redox state similar to Earth's, followed by CO, H₂O, and N₂ ⁸². When Earth cooled to temperatures which allowed liquid water, much of the atmospheric CO₂/CO dissolved into the new global ocean. Komatiite, a mafic to ultramafic igneous rock that paved the seafloor on early Earth, was exposed to this CO₂-enriched seawater and, as a result, underwent extensive mineral carbonation which caused an initial decrease in the CO₂-concentration of seawater and atmosphere ⁷⁸. Evidence of mineral carbonation is not limited to Earth. Carbonate-alteration of the Martian meteorites Lafayette and ALH84001 indicates that mineral carbonation likely occurred during the Noachian and Amazonian periods when liquid water was available on Mars's surface ^{103,104}. There are also signs of mineral carbonation on Ceres ¹⁰⁵. Therefore, similar processes can be expected to operate on habitable rocky exoplanets ^{106,107}

The speciation of gases during magmatic degassing is strongly influenced by atmospheric pressure 82 . For planets with similar bulk composition as Earth, while water may dominate the mix for pressures under \sim 3 bars, above that threshold, carbon dioxide is expected to dominate.

Current models therefore suggest that temperate terrestrial planets are able to produce a large (up to ~ 100 bars) CO₂ atmosphere via outgassing ^{82,108} and, if their surface temperature allows for water condensation, to sequester a large faction of it in their hydrosphere. If terrestrial exoplanets that underwent igneous differentiation expose Mg- and Fe-rich (mafic or ultramafic) lithologies to CO₂-rich fluids at temperatures lower than 300° C ¹⁰⁹, carbonate minerals can form at the expense of primary igneous minerals, such as olivine, which is the most abundant mineral in our Solar System. This process, referred to as mineral carbonation, is rapid on geological timescales ¹¹⁰.

It is possible that Venus was more similar to Earth during most of its history than it is presently. Current observations are compatible with Venus being both tectonically active and hosting habitable conditions on its surface as recently as 1 to 0.7 Gyr ago ^{111,112}. If this was the case, rising temperatures could have lead its surface liquid water bodies to evaporate and its hydrogen to escape to space, as evidenced by its D/H ratio ¹¹³. Since outgassed CO₂ dominates Venus' atmosphere, there would not have been an efficient carbonation process in place since. Observations are also compatible with Venus being never able to condense its water vapor into oceans ^{112,114,115}. In either scenario, relatively low carbon abundance in the atmosphere of a temperate rocky exoplanet, compared to other planets within the same system, appears as a reliable habsignature of recent and extensive amounts of liquid water at its surface.

Atmospheric carbon depletion as an habiosignature Atmospheric carbon depletion is a habiosignature because it can indicate the presence of a hydrosphere and/or of a biosphere, both planetshaping processes of interest to astronomers. A planet's concentration of CO₂ has long been known to be important to maintain its habitability. Research so far has focused on determining ${
m CO_2}$ concentrations which permit water to remain in a liquid phase at the surface, $^{6,106,116-118}$ in particular under the assumption of an Earth-like carbon cycle. For example, Refs. 116,118 propose empirical tests to the concept of the habitable zone, by making the hypothesis of having a population of terrestrial planet large enough to be able to statistically study how the CO₂ mixing ratio evolves with planet's insolations. Refs. 106,117 propose additional empirical tests by statistically studying how the CO₂ mixing ratio evolves between planets in and out of the Habitable Zone. Here, we take a complementary approach by considering that habitable planets will often have non-habitable neighbors. We argue that a terrestrial planet with an atmospheric carbon abundance orders of magnitude lower than others within the same system implies the presence of a hydrosphere and/or of a biosphere. Moreover, the water and carbon cycles are intertwined in a biological and geological context. Therefore, the concept of "habiosignature" might go further than semantics since Gaian cycles, a complex interplay of geological and biological processes ^{119–121}, are likely responsible for the relative long-term climate stability of our planet ^{120,122–124}, of which atmospheric carbon depletion is a tracer.

Whilst we argue that a depletion in atmospheric carbon is a habiosignature, we now focus more specifically on CO_2 (and thus a depletion in CO_2 , dCO_2) for most of the remainder of the

paper, primarily because of the ease of measuring its spectral features in the mid-infrared, and its applicability to rocky planets with compositions similar to Earth's.

Practical applications of detecting dCO₂. Systems with multiple terrestrial planets (with atmospheres) are needed before attempting to use dCO₂ as a hab- and habiosignature. As little as one additional terrestrial planet within the system might be sufficient. Here we stress that the more planets in a given system, and the closer they are to the planet being investigated, the better the calibration and thus the stronger the reliability of a depleted feature such as dCO₂. The physical properties of exoplanetary systems have low entropies, meaning that planetary systems are expected and found in "peas-in-a-pod" architectures ^{125–129}. Similarities between neighboring planets helps to calibrate depletions for a given planet. Proximity to the snow line could affect a planet's C/O ratio ¹³; however, this transition is not expected to lead to orders-of-magnitude differences in the initial carbon inventory, and C/O can be estimated from the atmospheric composition ^{2,12}.

Observations using direct imaging (e.g. using METIS with the ELT ¹³⁰) would be the most convenient. Compared to the transit method, it is more likely to identify all planets of a system, including those that might have a different redox state (having formed further from their star). Direct imaging is also a practical route to avoid a number of false positives and false negatives that we outline in Section 4. Unfortunately, the study of temperate rocky worlds via directing imaging remains out of reach to this day, whereas such planets are now accessible via

transmission spectroscopy.

Detectability of the dCO₂ habiosignature with JWST. Currently, JWST can search for dCO₂ for terrestrial planets transiting late-M dwarfs, which are expected to be abundant 131,132 . Figure 3 shows that detecting the presence of an atmospheric carbon depletion in the atmosphere of temperate terrestrial planet with JWST is within reach. Specifically, it shows that for a planet like TRAPPIST-1 f the mixing ratio of CO₂ can be constrained to within \sim 0.5 dex within 40 transits (Figure 3, middle). This results holds for planets TRAPPIST-1 e, g, and h, as they are expected to have a similar SNR to planet f, while the three innermost planets would require less than half that number of transits 41,46 . While elemental composition varies between different stellar systems (and between rocky planets from different star systems 133), within the same system planetary elemental composition are expected to be roughly similar 13,134 . This results in a capability to distinguish between high- and medium-depletion levels (respectively $X_{CO_2} = 400$ p.p.m. and $X_{CO_2} = 30\%$) at the $\sim 10\sigma$ level. It also allows to distinguish between medium- and negligible-depletion levels (respectively $X_{CO_2} = 10\%$ and $X_{CO_2} = 95\%$) at the $\sim 5\sigma$ level.

3 Three birds, one stone: observations of the $4.3~\mu\mathrm{m}$ CO $_2$ band

In addition to possibly yielding the detection of an habiosignature, the spectral range surrounding CO_2 's strong 4.3 μ m absorption band ¹³⁵ in the NIR offers observational benefits that support two other characterization steps: (1) the detection of atmospheres for terrestrial exoplanets,

and (2) the distinction between a biological and geological atmospheric carbon depletion.

Detecting the atmosphere of a temperate terrestrial exoplanet. To date, it has not yet been possible to reveal the presence of an atmosphere around a temperate terrestrial exoplanet, which is the very first step of atmospheric characterization. Up until now, it was only possible to search for hydrogen-dominated atmospheres using the *Hubble* Space Telescope ^{29–31,33,136}. Precise measurements of planetary physical parameters, notably transiting timing variations, can also constrain the presence/absence of a large hydrogen-dominated atmosphere ^{137,138}. JWST and the upcoming ELTs now offer the possibility to search for the presence of atmospheres for favorable terrestrial targets, such as the TRAPPIST-1 planets, in as little as 5 to 10 transits ^{41,47}. More transits, however, may be needed due to (1) stellar contamination of the planets' transmission spectra ^{139,140} and/or (2) the presence of clouds/hazes ^{47,137,141,142}.

We show in Figure 4 that there exists a sweet spot where the combination of both effects and the photon noise is optimal. The effect of stellar contamination decreases while photon noise increases beyond $\sim 1~\mu\mathrm{m}$ for stars like TRAPPIST-1. Therefore, a local minimum exists, dependent on the number of transits needed (photon noise). Figure 4 presents the uncertainty associated with the transmission spectrum of a TRAPPIST-1 planet gathered over 10 transits – the nominal amount for the reconnaissance of atmospheres around temperate terrestrial planets. To allow for an easy comparison we report the uncertainty at a uniform spectral resolving power of $R \sim 30$. The local minimum for such an exploration program is found between 4 and

 $10.5~\mu\mathrm{m}$. This wavelength range overlaps with the wavelength range over which hazes have a marginal impact on a planet's transmission spectrum, namely wavelengths above $\sim 3.3~\mu\mathrm{m}^{47}$ although the exact threshold depends on the aerosol size distribution.

The precision sweet spot for the reconnaissance of terrestrial planets with JWST via transmission spectroscopy thus lies between 4 and $10.5~\mu m$. In this spectral window, one absorption feature dominates across all models of secondary atmospheres contemplated in the literature: the CO₂ 4.3 μm band ^{47,137}. In fact, as shown in Figure 1, this band's absorption typically dominates absorption by molecules at shorter wavelengths as well.

 CO_2 absorption bands are of particular interest for atmospheric reconnaissance (i.e., a low SNR spectrum) as they are both strong and sharp. The bands are strong because CO_2 is an excellent absorber in the infrared ¹³⁵, even at a low atmospheric concentration (like in Earth's atmosphere). In fact, this molecular feature is the first reported by JWST in the atmosphere of an exoplanet ^{1,3,5}. CO_2 's bands are sharp and dense in opposition to, e.g., H_2O 's and CH_4 's broad and "sparse" absorption bands ¹³⁵. These two qualities of the CO_2 bands allow them to be more prominent in low-resolution spectra and thus not drowned out by correlated noise. As a result, the 4.3 μ m CO_2 band appears to be an optimal signature to detect the presence of secondary atmospheres around terrestrial planets, whilst being accessible to JWST and has been proposed for JWST observations already as a diagnostic test of the presence of a terrestrial planet atmospheres ¹⁴³.

Habitable or inhabited? Once an atmosphere has been detected around a temperate terrestrial exoplanet, we can reasonably expect that an extensive observing campaign will be dedicated to studying its atmospheric properties more in detail. For context, the atmospheric reconnaissance of the TRAPPIST-1 system initiated during JWST's Cycle 1 has already been supported by eight different observing programs, totaling over 200 hours. The scale of such a large characterization program will be capped to \sim 100 planetary transits, limited by the availability of windows of opportunity and by the telescope's lifetime. We use the TIERRA code ¹⁴⁴ to model planetary spectra and show that \sim 40 transits would be sufficient to yield constraints on the abundances of the dominant atmospheric absorbers. Figure 3 shows that the abundance of strong absorbers such as CO_2 can be constrained to within 0.5 dex, down to the 10 p.p.m. level (Earth's CO_2 concentration, for comparison, is 400 p.p.m.), thereby allowing to assess the presence of a habiosignature around planets like TRAPPIST-1's.

Assuming a habiosignature is revealed in the atmosphere of a temperate terrestrial planet, the next natural step will be to disentangle between a geological and biological origin, i.e., a habitable and inhabited environment. Is the observed dCO₂ driven mostly by a strong water cycle or also by biology? To answer this question, we evaluate the viability of two avenues that leverage the wavelength range surrounding the 4.3 μ m CO₂ band: (1) constraints on the isotopic fractionation of CO₂ and (2) constraints on the abundance of O₃.

Insights from isotopic fractionation Isotopic fractionation can be remotely detected ^{145,146}, owing to the fact that a change in a molecule's mass distribution results in shifts in its absorption lines. For CO_2 , the main difference in the 4.3 μ m band between the dominant isotopes ($^{12}C^{16}O_2$ and $^{13}C^{16}O_2$) is a substantial shift of the bandhead by $\sim 0.2 \mu$ m (Figure 5, left).

Isotopic fractionation is notably driven by atmospheric escape, biological activity, and water-rock interactions. In general, biological activity preferentially incorporates the light isotopes (e.g., 12 C and 1 H) into organic compounds; the removal of those organic compounds then drives the residual carbon toward heavier values. Plants and algae have approximate δ^{13} C values between -10 and -40×10^{-3} 147 and a δ^{2} H between -90 and -180×10^{-3} 148 .

Despite the presence of a global biology on Earth that contributes to about 20% of global carbon sequestration ⁸⁶, Earth's atmospheric carbon isotopic fractionation is consistent with other objects in the Solar System ¹⁴⁹. Similarly, Earth's rock record shows no substantial changes in ¹³C/¹²C over the last 3.5 billion years ^{150,151}, challenging our current understanding of isotope fractionation in extant metabolic pathways ¹⁵².

The picture further complexifies when one accounts for other sources of isotope fractionation that also favor the removal of light isotopes, such as atmospheric escape ^{153,154}. In addition to interpretation challenges, the detection of carbon fractionation in the atmosphere of a terrestrial planet will likely be out of reach with upcoming observatories. Figure 5 shows the expected contribution of ¹³CO₂ to be around the 5 p.p.m. level for an isotopic fraction similar

to Earth's atmosphere, and of \sim 15 p.p.m. level for $100\times$ Earth's. These values are smaller than the \sim 20 p.p.m. precision expected on such a spectral bin with \sim 100 transit observations (Figure 5, right panel). Therefore, carbon isotopologues are unlikely to be informative biosignatures for the JWST era 155 .

Insights from oxygen abundance While the sequestration of atmospheric CO_2 by a planet's hydrosphere allows for the removal of both carbon and oxygen $^{99-101}$, the sequestration of atmospheric CO_2 by a planet's biosphere leads primarily to the removal of just the carbon, leaving oxygen as a by-product 48,62 . For redox states similar to Earth's, CO_2 is expected to be the dominant molecule in the secondary atmospheres of terrestrial planets by orders of magnitude 82 . If CO_2 is depleted in a substantial manner by a photosynthetic biosphere, a large fraction of O_2 will consequently be returned to the atmosphere.

While O_2 is challenging to detect directly for known transiting exoplanets with upcoming observatories ^{43,53}, its presence can be inferred by detecting its photochemical byproduct O_3 ^{48,156–158}. Indeed, O_3 offers a series of strong absorption bands, similar to CO_2 , including one at 4.8 μ m ¹³⁵ in the vicinity of CO_2 's 4.3 μ m band. An Earth-equivalent level of ozone can readily be detected at the \sim 5- σ level with \sim 100 transits of TRAPPIST-1 f observed with JWST/NIRSpec (Fig. 5, right panel). This means that ozone concentrations down to the 10 p.p.m. level will be detectable for temperate terrestrial exoplanets with JWST ¹⁵⁹. We note that Earth's ozone level (10–15 p.p.m.) may serve as a lower limit considering the higher level

of stellar UV irradiation that temperate terrestrial exoplanets orbiting late M dwarfs will face, as they are the only terrestrial exoplanets amenable for atmospheric characterization with JWST 51.

 O_3 could also be produced via the photodissociation of CO_2 into CO and O_2 . However, only a small fraction of CO_2 is expected to be dissociated in such a way as seen for Venus and Mars (see next section) leaving an even smaller fraction of the resulting O_2 turned into O_3 . Thus, while the atmospheric depletion of CO_2 is an habiosignature preventing from distinguishing between the presence of a hydrosphere and a biosphere and that O_3 is an ambiguous biosignature just like O_2 , together, they form a reliable and readily accessible biomaker for the JWST era.

4 False positives & false negatives

Any signature has false positives and false negatives that can seriously impact the interpretation of a detected feature 48,49 , or in the present case, the identification of a depleted feature. However, we find that a depleted CO_2 (dCO_2) as a habiosignature has few such issues.

False positive scenarios A false positive to dCO_2 as a habiosignature would imply the detection of an atmosphere depleted in CO_2 without the contribution of a hydro- or a biosphere. We consider five such possible scenarios in the following.

• Dry Sequestration. Some rocks have a demonstrated ability to react with atmospheric

CO₂ and sequester it such as brucite, peridotite or serpentinite ¹¹⁰, which are considered for engineered carbon capture and sequestration to combat climate change. However, mineral carbonation of rocks is relatively inefficient when CO₂ is dry ¹⁶⁰, or if temperatures are low ($\ll 100^{\circ}$ C) ¹¹⁰. Reactions leading to carbon sequestration usually need access to water and the kinetics of all known carbon mineralization reactions currently occurring on Earth are greatly enhanced by water ¹⁶¹. For instance, brucite is one of most reactive minerals in the presence of CO₂ as long as water is available; brucite remains unreactive under a dry CO₂ atmosphere ¹⁶². The deep carbon cycle between the exosphere is critical in controlling atmospheric levels of CO₂ and the solid Earth operates on timescales $> 10^5$ years ¹⁰¹. However, the removal of CO_2 from the atmosphere is closely linked to the presence of water, either directly through the uptake of CO₂ in the surface ocean or indirectly via the dissolution of silicate minerals and precipitation of carbonate minerals. Using the Solar system as an example, even at high CO₂ fugacities, like on Venus, and high surface temperatures, CO₂ is stable in the atmosphere and demonstrates that dry carbonation of rocks has a likely minimal impact on carbon removal and is an unlikely false positive under dry conditions (Venus has lost most of its water ⁶⁰).

• Nightside Cold Trap. In a scenario of atmospheric collapse, most of the atmospheric CO₂ freezes on the night-side of a planet (tidally-locked or not) ¹⁶³, leaving low atmospheric CO₂ partial pressures in some cases ¹⁶⁴. Atmospheric collapse gets increasingly likely for planets further from their star. A collapse can be identified in some cases by

measuring an exoplanet's atmospheric temperature using transmission spectra. In addition, planets with measured atmospheric compositions compatible with this situation will need detailed and dedicated 3D numerical climate simulations to contextualize their CO_2 concentrations before any statement is made regarding their habitability. All the TRAPPIST-1 planets are expected to be tidally-locked ⁴⁶. For planets like TRAPPIST-1f, that we used in our simulations, atmospheric collapse is not expected for pressures typically $> 0.7 \, \text{bar}$, ¹⁶⁴.

• Photodissociation of CO₂. In this scenario, CO₂ is photo-dissociated or chemically transformed into other compounds. Our premise, however, is about atmospheric carbon abundance and not about just CO₂ abundance. The most likely carbon-bearing product from an atmospheric reaction involving CO₂ is CO ¹⁶⁵, which is also observable in the same 4 − 5 μm band (Figure 5) on which we encourage efforts to focus ⁵. As such, it is possible to measure the overall atmospheric carbon abundance with the same data. In any case, it is expected that at most 10% of CO₂ would transform into CO and O₂ ¹⁶⁵ for an atmosphere initially containing 1 bar of CO₂, which would be detectable with JWST (Figure 5). Atmospheres with higher partial pressures in initial CO₂ produce fractionally less CO ¹⁶⁶ as seen for instance on Venus. Furthermore, we advocate measuring and comparing several planets of the same system together since photo-dissociative effects are expected to decrease with orbital separation. Photo-dissociation is expected to decrease quadratically with distance from the star, in a monotonic function. As such we do not

expect order-of-magnitude differences between a series of adjacent planets, allowing a means to diagnose this process from others. The cases of Venus and Mars highlight that this is not a scenario of particular concern ¹⁶⁵.

- Photodissociation of other species Another aspect to consider relates to the production of ozone as a product of the photodissociation of stratospheric water. Refs. ^{167,168} have shown that slow-rotating terrestrial planets orbiting M dwarfs can have moist greenhouse conditions with significant levels of water vapor in their stratospheres. Late-M dwarfs such as TRAPPIST-1 are active longer into their life cycles and have stronger far-UV and weaker near-UV emissions, leading to exotic photochemistry ^{42,96,168–170}. This suggests that stratospheric water may produce a false positive detection of the biosignature dCO₂+O₃.
- **Reduced Interior.** A planet's atmospheric composition depends on whether its interior is oxidized or reduced ^{171,172}. In the latter case, instead of CO₂, CO and CH₄ are expected to be the main carbon carriers. Neither CO nor CH₄ dissolves well in liquid water, preventing carbon depletion via the hydrosphere. Planetary bulk compositions are expected to be increasingly reduced with orbital distance from their host star ¹⁷³, something that is also seen in the Solar system. Planets with different bulk compositions are also expected to outgas a different atmospheric chemistry ⁸². The detection of CO₂ in large concentrations for an outer planet indicates an oxidised world and would calibrate the inner system, and allow the detections of depleted feature on those planets. Disc-driven

migration is known to move planets from their birth place, and planetary objects similar to Titan, Triton and Pluto, assembled in Hydrogen-rich parts of the disc might be brought to the habitable zone $^{13,174-176}$. These objects have different bulk densities, and will be identified from their position in a mass/radius diagram 177 . In addition, should a temperate rocky planet be in a reduced state, this can be easily diagnosed from their atmospheric composition 177,178 . CO would show a prominent feature in the same $4-5~\mu\mathrm{m}$ range with CO₂ absent (Figure 5, right panel). CH₄ has an absorption band at 3.3 $\mu\mathrm{m}$, likely to be observed with the same instrumental setup. Both the CO and the CH₄ features present higher level of significance than CO₂'s. For reduced sets of planets, a different set of bio and habsignature would need to be found.

• Other Surface Solvent. In this scenario, an abundant liquid solvent other than liquid water is able to dissolve and sequester carbon efficiently at room temperature. CO₂ is soluble in other liquids such as ethanol (alcohols) or polyethylene glycol ^{179,180} but, to our knowledge, such compounds do not form abiotically in significant amounts on a planetary scale. Liquid methane is a fairly efficient solvent for CO₂ ¹⁸¹ that can form in large amounts on a planetary scale, for instance, Titan's lakes. However, liquid CH₄ is only stable at extremely low temperatures (~ 120 K) that are not habitable for life as we know it. Water remains one of the most abundant molecules in the Universe, and the most abundant solvent expected to be outgassed and condensed for a temperate terrestrial planet ⁸².

From their very first detections, exoplanets' orbital and physical properties have defied expectations ^{182–185}. We have tried to explore many false positive signatures, but unknown and efficient CO₂ removal processes could well operate on an exoplanet. In this event, the detection of an atmospheric carbon depletion would not be attributed to the presence of a hydrosphere or a biosphere, but it would reveal an unexpected sequestration mechanism efficient on a planetary scale. This depleted feature would thus still be of very high scientific interest and could possibly spark novel industrial exploration of processes capable of balancing anthropogenic emissions of CO₂, and address climate change on Earth. More research is needed to understand how atmospheric carbon reacts with different solvents, at different temperatures and pressures, how photochemistry in terrestrial planet atmospheres around M dwarfs work while considering different bulk compositions, as well as to study the possible nature and availability of such solvent alternatives.

False negative scenarios A false negative is a planet that possesses large amounts of liquid water and/or a biosphere, but its atmosphere is not depleted in CO_2 . We consider three such possible scenarios in the following.

• **Subsurface Biosphere.** An atmosphereless planet can be habitable in its interior if habitability is defined to also include sub-surface liquid water. Such a situation is similar to Europa and Enceladus ^{186,187}. In this particular case, this is an issue of definition. An atmospheric signature is only valid where there is a detectable atmosphere. Other planets

might present low atmospheric pressures that are hard to detect, similar to the case of Mars. Those cases will be noticed easily. From their already known radius and/or the mass it is possible to deduce a past atmospheric escape.

- Saturated Oceans. Depleted CO₂ as a habsignature only functions if carbon continuously dissolves into the ocean. Plate tectonics moves the crust about and, in doing so, moves carbonates outside of oceans onto land, which we can see nowadays as limestone deposits. Tectonics also mostly buries carbonates out of reach of the atmosphere into the crust and back into the mantle ^{78,86,188}. A false negative could emerge for rocky exoplanets without plate tectonics, and/or where the oceans become saturated and can no longer absorb any more CO₂ 102,189,190. Without other known efficient sinks, CO₂ would therefore remain in the atmosphere. Should this scenario happen, other widely used biosignatures can still be employed, and used in exactly the same way as they are being considered nowadays. However, whilst the onset of plate tectonics is still a highly debated topic ^{191,192}, it is generally accepted that liquid water is required to weaken the protoplates' yield stress ^{193,194}, and that liquid water and carbonates lubricate the plates' motion. This means that tectonics might be an inevitability of a habitable/inhabited world ^{60,119,120}. For packed, close-in systems of exoplanets, such as the TRAPPIST-1 system ⁴⁶, plate tectonics might also be initiated tidally ¹⁹⁵, or via impacts ^{196,197}.
- Transient CO₂ concentration. In this scenario, an extensive liquid water ocean is present but has not had time yet to significantly remove enough atmospheric carbon for a detec-

tion. The Archean Earth represents such a transition period. Yet, as discussed in Section 2, dCO₂ was detectable as a habsignature during most of the eon (Fig. 3). However as biomarker, it would likely be inconclusive since Earth was dominated at the time by methanogens $^{71.80}$, as we consider oxic biospheres (like the modern Earth) in this study. Earth's oceans contain about 2 bars of CO₂ currently $^{77.79}$. If released in the atmosphere, the oceans would absorb those 2 bars of CO₂ in ~ 0.2 Gyr, at current absorption rates $^{80.86,101}$. Indeed, it is thought that most of Earth's primordial atmospheric CO₂ was dissolved by the time biological processes emerged on Earth circa 0.5 Gyr after formation $^{78.80}$. This makes this false negative scenario likely to be observed in less than 1 in 50 habitable rocky planets. We note here that this scenario might be a faux- false negative, as a sudden release of bars of CO₂ (that could equally be produced by other events such as asteroid/comet impacts, or extensive volcanic episodes) would trigger a substantial temperature increase due to greenhouse effects 116,117 , thus reducing the habitability and inhabited nature of the planet temporarily.

• Habitability near the outer edge. A planet near the outer edge of the habitable zone requires an important CO_2 partial pressure to maintain habitable conditions at the surface 6,60,116-118. For instance, moving Earth to the orbit of Mars requires about 2 bars of CO_2 to keep water in a liquid state. Our simulations (Fig. 3) show such a scenario is difficult to distinguish. After collecting 40 transits with JWST, any concentrations > 50% CO_2 do not produce spectra significantly different ($< 3\sigma$) than those from atmospheres with

 $100\%~\mathrm{CO_2}.$ Other habsignatures will need to be deployed for those cases.

5 Summary and future prospects

Life on Earth is obvious. It shapes most aspects of our environment, including the composition of the atmosphere above us, and of the ocean and rocks below us ^{119,122}. Its continuity across several billion years is likely regulated by Gaian cycles, a complex system of geological, atmospheric and biological balances understood and nowadays investigated as "Earth's systems" ^{119–121}. Life on Earth has a truly global effect. In other words, Life on Earth is planet-shaping. Planet-shaping Life is really what astronomers are after ¹²¹. Should Life have arisen on Venus ¹⁹⁸, on Mars ¹⁹⁹, Europa ²⁰⁰ or Enceladus ²⁰¹, whilst extremely fascinating, it is clearly not as planet-shaping, simply because it is not nearly as obvious in affecting what can be observed and measured about these celestial objects. Such Life would not be detectable on exoplanets, whereas planet-shaping Life is.

In this perspective, we outline how atmospheric carbon depletion, particular a carbon dioxide depletion, is a logical tracer of planet-shaping Life, and is able to reveal its global impact using remote-sensing methods of observation. An atmosphere such as Earth's becomes depleted in carbon thanks to the action of extensive amounts of surface liquid water, and/or by intense biological processes. Plate tectonics buries carbon away from the atmosphere, causing atmospheric depletion of CO₂ over geological timescales ¹⁸⁸.

In much of the scientific literature, observables are appreciated as a signal, an addition to something otherwise presumed pristine. For exoplanets, tracers of habitability –habsignatures–

such as the glint of a surface ocean ⁶², and tracers of biology –biosignatures– such as O₂ in quantities beyond those expected by photodissociation and chemical equilibrium ^{48,49,122}, are all added signals. However, planet-shaping Life does not just produce but also consumes ⁸¹, and the Earth's systems that sustain it (e.g. liquid water) also actively remove chemical species from the atmosphere ^{99–101}. We believe it is just as important to consider depleted signals as habsignatures and biosignatures. In the context of atmospheric carbon depletion, a depleted CO₂ feature compared to other planets within the same system is a good habiosignature, as it traces both habitable and inhabited environments. We explored the likelihood of false positive found all those we could imagine were unlikely to exist. We also investigated false negative signals, and propose means of addressing them. This is why we assess that CO₂ depletion is a robust habiosignature applicable to most temperate rocky exoplanets, particularly those most similar to Earth.

Measuring the CO_2 absorption feature comes with multiple benefits. Even at low concentrations, CO_2 absorption is the most detectable of all atmospheric features for a transiting temperate terrestrial exoplanet and can reveal whether the planet has an atmosphere, the first step in the characterization of any exohabitats. Furthermore, CO_2 is located at wavelengths where contamination from clouds and hazes is minimal, and where stellar contamination decreases below the typical photon noise, even for highly active late- M dwarfs. At these wavelengths, other molecules of interest have features too: CH_4 , CO, and O_3 , all of which are relevant in assessing the carbon abundance of the atmosphere, and in the case of O_3 , in distinguishing whether

carbon depletion is produced only by an ocean, or also by biology.

These facts lead us to propose an observational strategy: to target the CO_2 feature, first with a few planetary transits, in order to assess the presence of an atmosphere and obtain an initial estimate of CO_2 concentration on several planets of the same system. Should these reconnaissance observations reveal depleted CO_2 features, these observations need to be augmented with a more extensive observing campaign, that will accurately measure their CO_2 abundances, but also the presence and concentrations of CH_4 , CO, and O_3 .

We sincerely hope this strategy is implemented by the multiple teams around the world that are attempting to explore the atmospheres of transiting temperate rocky exoplanets using space-based observatories like JWST, but also planning to use ground-based facilities such as the upcoming Extremely Large Telescopes. We also encourage all teams to investigate other depleted molecular features and bring about new tracers of habitability and biological activity. The more we have, the more reliable our interpretations of temperate rocky exoplanet spectra will be.

6 Captions of Figures

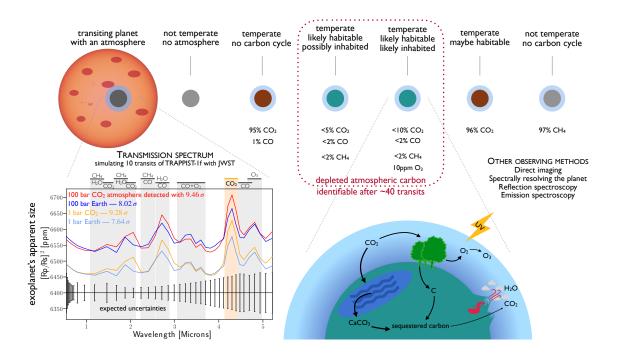


Figure 1: Illustration of our strategy to detect habitable exoplanetary environment via CO_2 depletion. Each of the planets to the right hand side of the star describes a different scenario discussed in the text (along with illustrative atmospheric concentrations). The panel on the left hand side depicts a simulation of the transmission spectrum of the temperate terrestrial planet TRAPPIST-1 f. We explore the detectability of an atmosphere with ~ 10 JWST/NIRSpec Prism transit observations, the minimum needed to produce a reliable diagnostic. Note that the deviation from a flat signal (no atmosphere) is primarily supported by the strong absorption features of CO_2 , notably at 4.3 μ m (highlighted). Exo-atmospheric models from ¹⁴⁴ were used to make that panel. On the lower right hand side, we illustrate a simplified view of a carbon cycle involving surface liquid water and biology sequestering cycle and producing a depletion in atmospheric carbon. Atmospheric concentrations given near the planets are illustrative.

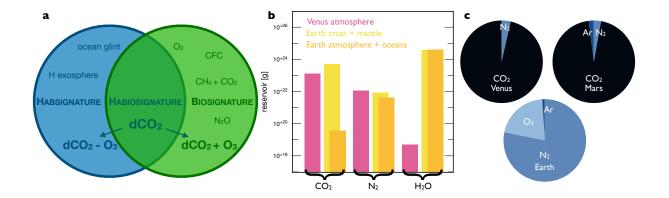


Figure 2: CO₂ depletion ("dCO₂") as a signature of liquid water and/or life. Left: Schematic representation of observables associated with the presence of surface liquid water ("habsignature"), of a biomass ("biosignature"), or both ("habiosignature"). Centre: Comparison between present day Venus's, and Earth's interior and atmospheric volatile inventories (Data from Ref.⁷⁵). Right: relative atmospheric abundances for Venus, Earth and Mars.

Correspondence Correspondence and requests for materials should be addressed to A.H.M.J.T (email: a.triaud@bham.ac.uk) and J.d.W (email: jdewit@mit.edu).

Acknowledgements Authors thank M. Gillon and A. Babbin for insightful discussions. B.V.R. thanks the Heising-Simons Foundation for support. AHMJT's research received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement n° 803193/BEBOP).

Author Contributions

A.H.M.J.T. and J.d.W. produced the main concepts and led the team behind this Perspective. Every author contributed to the writing of this manuscript. F.K., M.T., O.E.J. and M.P. focused their contribution

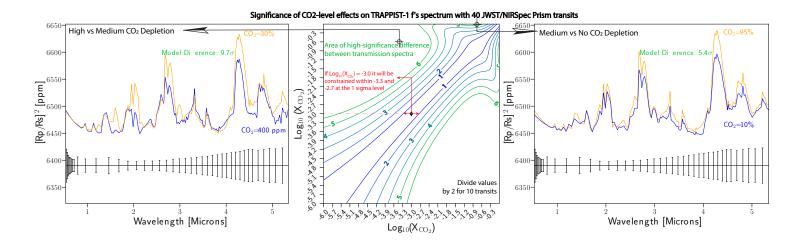


Figure 3: Detectability of CO_2 depletion ("d CO_2 ") as an habiosignature with JWST. Middle: Significance map of CO_2 -level effects on TRAPPIST-1 f's spectrum with 40 JWST/NIRSpec Prism transits. Values reported represented the deviation between two transmission spectra with different concentration of CO_2 (X_{CO_2}). The region around the 1:1 line surrounded by the 1- σ contour is at low-significance. The width of that region represents the confidence interval with which a given X_{CO_2} can be retrieved (typically ~ 0.5 dex, example provided in orange for Log_{10} ($X_{CO_2} = -3.0$)). Left: Comparison between the spectra of TRAPPIST-1 f with a high CO_2 depletion ($X_{CO_2} = 400$ p.p.m.) and medium one ($X_{CO_2} = 30\%$). The spectra and their associated 1- σ errorbar (black) are shown for a resolving power of $R \sim 30$. Right: Comparison between the spectra of TRAPPIST-1 f with a medium CO_2 depletion ($X_{CO_2} = 10\%$) and without any ($X_{CO_2} = 95\%$).

to the geological discussion of the paper. M.T., J.J.P., A.G., S.S., and F.S. particularly contributed to the atmospheric and biosignature aspects of the paper. B.V.R. and P.N. mostly contributed to the discussion

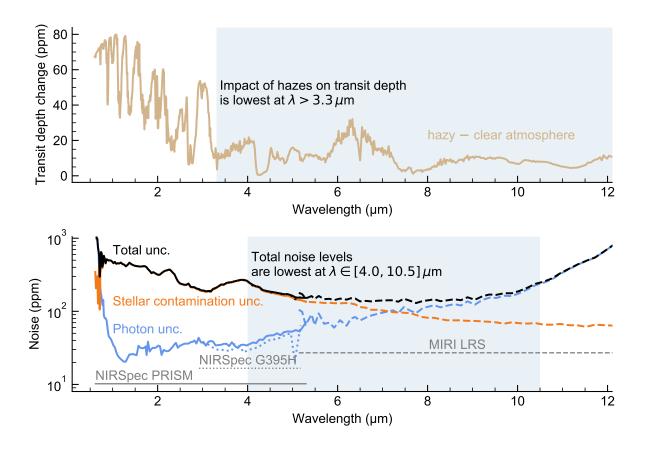


Figure 4: Top: The difference between "hazy" and "clear atmosphere" transmission spectra for TRAPPIST-1e ⁴⁷. The impact of haze on the transit depth is smallest at wavelengths greater than 3.3 μ m. Bottom: Photon-limited uncertainties increase at the shortest and longest wavelengths, where the photon flux from the star is limited. Systematic uncertainty due to stellar contamination increases toward shorter wavelengths, where contrasts between spots and faculae with respect to the photosphere are greatest. The combined uncertainty from these noise sources reaches a minimum between 4–10.5 μ m. See details in Code Availability section.

and figures related to observational aspects.

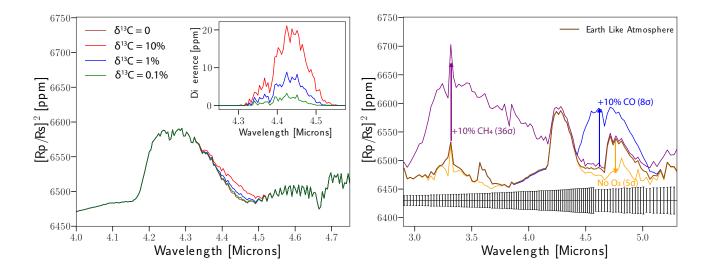


Figure 5: Disentangling between the water- or life-based origin of a CO₂-depletion ("dCO₂") habiosignature. Left: Effect of different 13 C-to- 12 C ratios (δ^{13} C) on TRAPPIST-1 f transmission spectrum. Effects seen are limited to up to 15ppm, implying that the detecting the isotopic fractionation of carbon in the atmosphere of a temperate terrestrial planet with JWST is out of reach (requires >300 transits). Right: Effect of O₃ depletion and CH₄ and CO 10% enrichment on TRAPPIST-1 f transmission spectrum. The spectra and their associated 1- σ errorbar (black) are shown for a resolving power of R \sim 130. Detecting ozone in the atmosphere of a temperate terrestrial planet would support the biological origin of a CO₂ habiosignature and is within reach with \sim 100 JWST transit observations.

Competing Interests The authors declare that they have no competing financial interests.

Data Availability n/a

Code Availability The JWST photon uncertainties in Figure 4 are calculated using PandExo ²⁰². Sys-

tematic uncertainties due to stellar contamination are calculated via a Monte Carlo approach using the temperatures and covering fractions of the two dominant photospheric components inferred from HST observations ³³. We allow the covering fraction of the lesser component to vary uniformly from 0% to double the reported covering fraction, calculate the corresponding stellar contamination signal following ref. ¹⁴⁰, and report the standard deviation of the contamination signal for 10,000 such realizations as the systematic uncertainty. We draw the component spectra from the DRIFT-PHOENIX grid ²⁰³ using speclib^{1 204}. The total uncertainties are the quadrature sums of the photon and systematic uncertainties. TIERRA² is a publicly available 1D transmission model written in python. It was originally introduced in ref¹⁴⁴ and has been used to create transmission spectra models for Earth-like atmospheres assuming isothermal profiles in Figure 1, Figure 3 and Figure 5.

References

- JWST Transiting Exoplanet Community Early Release Science Team *et al*. Identification of carbon dioxide in an exoplanet atmosphere. *Nature* 614, 649–652 (2023). 2208.
 11692.
- 2. Ahrer, E.-M. *et al.* Early Release Science of the exoplanet WASP-39b with JWST NIR-Cam. *Nature* **614**, 653–658 (2023). 2211.10489.
- 3. Alderson, L. *et al.* Early Release Science of the exoplanet WASP-39b with JWST NIR-Spec G395H. *Nature* **614**, 664–669 (2023). 2211.10488.

https://github.com/brackham/speclib

²https://github.com/disruptiveplanets/tierra

- 4. Feinstein, A. D. *et al.* Early Release Science of the exoplanet WASP-39b with JWST NIRISS. *Nature* **614**, 670–675 (2023). 2211.10493.
- 5. Rustamkulov, Z. *et al.* Early Release Science of the exoplanet WASP-39b with JWST NIRSpec PRISM. *Nature* **614**, 659–663 (2023). 2211.10487.
- Krissansen-Totton, J., Thompson, M., Galloway, M. L. & Fortney, J. J. Understanding planetary context to enable life detection on exoplanets and test the Copernican principle.
 Nature Astronomy 6, 189–198 (2022). 2202.10333.
- 7. Deming, L. D. & Seager, S. Illusion and reality in the atmospheres of exoplanets. *Journal of Geophysical Research (Planets)* **122**, 53–75 (2017).
- 8. Seager, S. & Sasselov, D. D. Theoretical Transmission Spectra during Extrasolar Giant Planet Transits. *Astrophys. J.* **537**, 916–921 (2000). astro-ph/9912241.
- 9. Brown, T. M. Transmission Spectra as Diagnostics of Extrasolar Giant Planet Atmospheres. *Astrophys. J.* **553**, 1006–1026 (2001). astro-ph/0101307.
- 10. Hubbard, W. B. *et al.* Theory of Extrasolar Giant Planet Transits. *Astrophys. J.* **560**, 413–419 (2001). astro-ph/0101024.
- 11. de Wit, J. & Seager, S. Constraining Exoplanet Mass from Transmission Spectroscopy. *Science* **342**, 1473–1477 (2013). 1401.6181.

- 12. Madhusudhan, N. Exoplanetary Atmospheres: Key Insights, Challenges, and Prospects. *Annual Review of Astronomy and Astrophysics* **57**, 617–663 (2019). 1904.03190.
- 13. Öberg, K. I., Murray-Clay, R. & Bergin, E. A. The Effects of Snowlines on C/O in Planetary Atmospheres. *Astrophys. J., Letters* **743**, L16 (2011). 1110.5567.
- Pinhas, A., Madhusudhan, N., Gandhi, S. & MacDonald, R. H₂O abundances and cloud properties in ten hot giant exoplanets. *Mon. Not. R. Astron. Soc.* 482, 1485–1498 (2019).
 1811.00011.
- 15. Wyttenbach, A. *et al.* Mass-loss rate and local thermodynamic state of the KELT-9 b thermosphere from the hydrogen Balmer series. *Astron. Astrophys.* **638**, A87 (2020). 2004.13733.
- Mollière, P. & Snellen, I. A. G. Detecting isotopologues in exoplanet atmospheres using ground-based high-dispersion spectroscopy. *Astron. Astrophys.* 622, A139 (2019).
 1809.01156.
- 17. Zhang, Y. *et al.* The ¹³CO-rich atmosphere of a young accreting super-Jupiter. *Nature* **595**, 370–372 (2021). 2107.06297.
- 18. Snellen, I. A. G., de Kok, R. J., de Mooij, E. J. W. & Albrecht, S. The orbital motion, absolute mass and high-altitude winds of exoplanet HD209458b. *Nature* **465**, 1049–1051 (2010). 1006.4364.

- 19. Louden, T. & Wheatley, P. J. Spatially Resolved Eastward Winds and Rotation of HD 189733b. *Astrophys. J., Letters* **814**, L24 (2015). 1511.03689.
- 20. Wyttenbach, A. *et al.* Hot Exoplanet Atmospheres Resolved with Transit Spectroscopy (HEARTS). I. Detection of hot neutral sodium at high altitudes on WASP-49b. *Astron. Astrophys.* **602**, A36 (2017). 1702.00448.
- 21. Spake, J. J. *et al.* Helium in the eroding atmosphere of an exoplanet. *Nature* **557**, 68–70 (2018). 1805.01298.
- 22. Knutson, H. A. *et al.* A map of the day-night contrast of the extrasolar planet HD 189733b. *Nature* **447**, 183–186 (2007). 0705.0993.
- 23. Cowan, N. B. *et al.* Alien Maps of an Ocean-bearing World. *Astrophys. J.* **700**, 915–923 (2009). 0905.3742.
- 24. Majeau, C., Agol, E. & Cowan, N. B. A Two-dimensional Infrared Map of the Extrasolar Planet HD 189733b. *Astrophys. J., Letters* **747**, L20 (2012). 1202.1883.
- 25. de Wit, J., Gillon, M., Demory, B. O. & Seager, S. Towards consistent mapping of distant worlds: secondary-eclipse scanning of the exoplanet HD 189733b. *Astron. Astrophys.* **548**, A128 (2012). 1202.3829.
- 26. Challener, R. C. & Rauscher, E. ThERESA: Three-dimensional Eclipse Mapping with Application to Synthetic JWST Data. *Astron. J.* **163**, 117 (2022). 2110.08159.

- 27. Sing, D. K. *et al.* A continuum from clear to cloudy hot-Jupiter exoplanets without primordial water depletion. *Nature* **529**, 59–62 (2016). 1512.04341.
- 28. Mansfield, M. *et al.* Confirmation of Water Absorption in the Thermal Emission Spectrum of the Hot Jupiter WASP-77Ab with HST/WFC3. *Astron. J.* **163**, 261 (2022). 2203. 01463.
- 29. de Wit, J. *et al.* A combined transmission spectrum of the Earth-sized exoplanets TRAPPIST-1 b and c. *Nature* **537**, 69–72 (2016). 1606.01103.
- 30. de Wit, J. *et al.* Atmospheric reconnaissance of the habitable-zone Earth-sized planets orbiting TRAPPIST-1. *Nature Astronomy* **2**, 214–219 (2018). 1802.02250.
- 31. Wakeford, H. R. *et al.* Disentangling the Planet from the Star in Late-Type M Dwarfs: A Case Study of TRAPPIST-1g. *Astron. J.* **157**, 11 (2019). 1811.04877.
- 32. Kreidberg, L. *et al.* Absence of a thick atmosphere on the terrestrial exoplanet LHS 3844b.

 Nature 573, 87–90 (2019). 1908.06834.
- 33. Garcia, L. J. *et al.* HST/WFC3 transmission spectroscopy of the cold rocky planet TRAPPIST-1h. *Astron. Astrophys.* **665**, A19 (2022). 2203.13698.
- 34. Dransfield, G. & Triaud, A. H. M. J. Colour-magnitude diagrams of transiting exoplanets
 III. A public code, nine strange planets, and the role of phosphine. *Mon. Not. R. Astron.*Soc. 499, 505–519 (2020). 2008.00995.

- 35. Fauchez, T. J. et al. TRAPPIST Habitable Atmosphere Intercomparison (THAI) Workshop Report. *The Planetary Science Journal* **2**, 106 (2021).
- 36. Felton, R. C. *et al.* The Role of Atmospheric Exchange in False-Positive Biosignature Detection. *Journal of Geophysical Research (Planets)* **127**, e06853 (2022). 2206.00028.
- 37. Turbet, M. *et al.* The TRAPPIST-1 Habitable Atmosphere Intercomparison (THAI). I. Dry Cases-The Fellowship of the GCMs. *The Planetary Science Journal* **3**, 211 (2022). 2109.11457.
- 38. Sergeev, D. E. et al. The TRAPPIST-1 Habitable Atmosphere Intercomparison (THAI).
 II. Moist Cases-The Two Waterworlds. The Planetary Science Journal 3, 212 (2022).
 2109.11459.
- 39. Morley, C. V., Kreidberg, L., Rustamkulov, Z., Robinson, T. & Fortney, J. J. Observing the Atmospheres of Known Temperate Earth-sized Planets with JWST. *Astrophys. J.* **850**, 121 (2017). 1708.04239.
- 40. Malik, M. *et al.* Analyzing Atmospheric Temperature Profiles and Spectra of M Dwarf Rocky Planets. *Astrophys. J.* **886**, 142 (2019). 1907.13135.
- 41. Lustig-Yaeger, J., Meadows, V. S. & Lincowski, A. P. The Detectability and Characterization of the TRAPPIST-1 Exoplanet Atmospheres with JWST. *Astron. J.* **158**, 27 (2019). 1905.07070.

- 42. Wunderlich, F. *et al.* Detectability of atmospheric features of Earth-like planets in the habitable zone around M dwarfs. *Astron. Astrophys.* **624**, A49 (2019). 1905.02560.
- 43. Fauchez, T. J. *et al.* Sensitive probing of exoplanetary oxygen via mid-infrared collisional absorption. *Nature Astronomy* **4**, 372–376 (2020). 2001.01361.
- 44. Pidhorodetska, D., Fauchez, T. J., Villanueva, G. L., Domagal-Goldman, S. D. & Kopparapu, R. K. Detectability of Molecular Signatures on TRAPPIST-1e through Transmission Spectroscopy Simulated for Future Space-based Observatories. *Astrophys. J., Letters* 898, L33 (2020). 2001.01338.
- 45. Fauchez, T. J. *et al.* The TRAPPIST-1 Habitable Atmosphere Intercomparison (THAI). III. Simulated Observables-the Return of the Spectrum. *The Planetary Science Journal* 3, 213 (2022). 2109.11460.
- 46. Gillon, M. *et al.* Seven temperate terrestrial planets around the nearby ultracool dwarf star TRAPPIST-1. *Nature* **542**, 456–460 (2017). 1703.01424.
- 47. Fauchez, T. J. *et al.* Impact of Clouds and Hazes on the Simulated JWST Transmission Spectra of Habitable Zone Planets in the TRAPPIST-1 System. *Astrophys. J.* **887**, 194 (2019). 1911.08596.
- 48. Meadows, V. S. *et al.* Exoplanet Biosignatures: Understanding Oxygen as a Biosignature in the Context of Its Environment. *Astrobiology* **18**, 630–662 (2018). 1705.07560.

- 49. Catling, D. C. *et al.* Exoplanet Biosignatures: A Framework for Their Assessment. *Astrobiology* **18**, 709–738 (2018). 1705.06381.
- 50. Nutzman, P. & Charbonneau, D. Design Considerations for a Ground-Based Transit Search for Habitable Planets Orbiting M Dwarfs. *Publ. Astron. Soc. Pacific* **120**, 317 (2008). 0709.2879.
- 51. Triaud, A. H. M. J. Small Star Opportunities. In Madhusudhan, N. (ed.) *ExoFrontiers;*Big Questions in Exoplanetary Science, 6–1 (2021).
- 52. Snellen, I. A. G., de Kok, R. J., le Poole, R., Brogi, M. & Birkby, J. Finding Extraterrestrial Life Using Ground-based High-dispersion Spectroscopy. *Astrophys. J.* **764**, 182 (2013). 1302.3251.
- 53. Rodler, F. & López-Morales, M. Feasibility Studies for the Detection of O₂ in an Earth-like Exoplanet. *Astrophys. J.* **781**, 54 (2014). 1312.1585.
- 54. Serindag, D. B. & Snellen, I. A. G. Testing the Detectability of Extraterrestrial O₂ with the Extremely Large Telescopes Using Real Data with Real Noise. *Astrophys. J., Letters* **871**, L7 (2019). 1901.02469.
- 55. Leung, M., Meadows, V. S. & Lustig-Yaeger, J. High-resolution Spectral Discriminants of Ocean Loss for M-dwarf Terrestrial Exoplanets. *Astron. J.* **160**, 11 (2020). 2004.13731.
- 56. Webb, R. K. Exoplanet atmospheres at high spectral resolution in the near-infrared (2023).

 URL http://wrap.warwick.ac.uk/1416751/.

- 57. López-Morales, M. *et al.* Optimizing Ground-based Observations of O₂ in Earth Analogs. *Astron. J.* **158**, 24 (2019). 1905.05862.
- 58. Marconi, A. *et al.* ANDES, the high resolution spectrograph for the ELT: science case, baseline design and path to construction. In Evans, C. J., Bryant, J. J. & Motohara, K. (eds.) *Ground-based and Airborne Instrumentation for Astronomy IX*, vol. 12184 of *Society of Photo-Optical Instrumentation Engineers (SPIE) Conference Series*, 1218424 (2022).
- 59. Lovis, C. *et al.* Atmospheric characterization of Proxima b by coupling the SPHERE high-contrast imager to the ESPRESSO spectrograph. *Astron. Astrophys.* **599**, A16 (2017). 1609.03082.
- 60. Kasting, J. F., Whitmire, D. P. & Reynolds, R. T. Habitable Zones around Main Sequence Stars. *Icarus* **101**, 108–128 (1993).
- 61. Kopparapu, R. K., Wolf, E. T. & Meadows, V. S. Characterizing Exoplanet Habitability. In Meadows, V. S., Arney, G. N., Schmidt, B. E. & Des Marais, D. J. (eds.) *Planetary Astrobiology*, 449 (2020).
- 62. Sagan, C., Thompson, W. R., Carlson, R., Gurnett, D. & Hord, C. A search for life on Earth from the Galileo spacecraft. *Nature* **365**, 715–721 (1993).
- 63. Stephan, K. et al. Specular reflection on Titan: Liquids in Kraken Mare. Geophysics Research Letters 37, L07104 (2010).

- 64. Lustig-Yaeger, J. *et al.* Detecting Ocean Glint on Exoplanets Using Multiphase Mapping. *Astron. J.* **156**, 301 (2018). 1901.05011.
- 65. Kameda, S. *et al.* Ecliptic North-South Symmetry of Hydrogen Geocorona. *Geophysics Research Letters* **44**, 11,706–11,712 (2017).
- 66. dos Santos, L. A., Bourrier, V., Ehrenreich, D. & Kameda, S. Observability of hydrogenrich exospheres in Earth-like exoplanets. *Astron. Astrophys.* **622**, A46 (2019). 1812.
- 67. Elkins-Tanton, L. T. & Seager, S. Coreless Terrestrial Exoplanets. *Astrophys. J.* **688**, 628–635 (2008). 0808.1908.
- 68. Loftus, K. *et al.* Sulfate Aerosol Hazes and SO₂ Gas as Constraints on Rocky Exoplanets' Surface Liquid Water. *Astrophys. J.* **887**, 231 (2019). 1908.02769.
- 69. Jordan, S. *et al.* Photochemistry of Venus-like Planets Orbiting K- and M-dwarf Stars. *Astrophys. J.* **922**, 44 (2021). 2108.05778.
- 70. Mendillo, M., Withers, P. & Dalba, P. A. Atomic oxygen ions as ionospheric biomarkers on exoplanets. *Nature Astronomy* **2**, 287–291 (2018).
- 71. Krissansen-Totton, J., Olson, S. & Catling, D. C. Disequilibrium biosignatures over Earth history and implications for detecting exoplanet life. *Science Advances* **4**, eaao5747 (2018). 1801.08211.

- 72. Villanueva, G. L., Mumma, M. J. & Magee-Sauer, K. Ethane in planetary and cometary atmospheres: Transmittance and fluorescence models of the ν_7 band at 3.3 μ m. *Journal of Geophysical Research (Planets)* **116**, E08012 (2011).
- 73. Haqq-Misra, J., Fauchez, T. J., Schwieterman, E. W. & Kopparapu, R. Disruption of a Planetary Nitrogen Cycle as Evidence of Extraterrestrial Agriculture. *Astrophys. J.*, *Letters* **929**, L28 (2022). 2204.05360.
- 74. Schwieterman, E. W. *et al.* Evaluating the Plausible Range of N₂O Biosignatures on Exo-Earths: An Integrated Biogeochemical, Photochemical, and Spectral Modeling Approach. *Astrophys. J.* **937**, 109 (2022). 2210.01669.
- van Thienen, P. et al. Water, Life, and Planetary Geodynamical Evolution. In Fishbaugh,
 K. E., Lognonné, P., Raulin, F., Des Marais, D. J. & Korablev, O. (eds.) Geology and
 Habitability of Terrestrial Planets, vol. 24, 167 (2007).
- 76. Walker, J. C. G. Carbon dioxide on the early earth. *Origins of Life* **16**, 117–127 (1985).
- 77. Pierrehumbert, R. T. Principles of Planetary Climate (2010).
- 78. Shibuya, T. *et al.* Decrease of seawater co2 concentration in the late archean: An implication from 2.6ga seafloor hydrothermal alteration. *Precambrian Research* **236**, 59–64 (2013). URL https://www.sciencedirect.com/science/article/pii/S0301926813002210.

- 79. Lécuyer, C., Simon, L. & Guyot, F. Comparison of carbon, nitrogen and water budgets on Venus and the Earth. *Earth and Planetary Science Letters* **181**, 33–40 (2000).
- 80. Catling, D. C. & Zahnle, K. J. The Archean atmosphere. *Science Advances* **6**, eaax1420 (2020).
- 81. Sethi, D., Butler, T., Shuhaili, F. & Vaidyanathan, V. Diatoms for Carbon Sequestration and Bio-Based Manufacturing. *Biology (Basel)* **9**, 217 (2020).
- 82. Gaillard, F. *et al.* The Diverse Planetary Ingassing/Outgassing Paths Produced over Billions of Years of Magmatic Activity. *Space Science Reviews* **217**, 22 (2021).
- 83. Archer, D. E. An atlas of the distribution of calcium carbonate in sediments of the deep sea. *Global Biogeochemical Cycles* **10**, 159–174 (1996).
- 84. Bednaršek, N., Možina, J., Vogt, M., O'Brien, C. & Tarling, G. A. The global distribution of pteropods and their contribution to carbonate and carbon biomass in the modern ocean. *Earth System Science Data* **4**, 167–186 (2012).
- 85. Archer, D. et al. Atmospheric Lifetime of Fossil Fuel Carbon Dioxide. Annual Review of Earth and Planetary Sciences 37, 117–134 (2009).
- 86. Plank, T. & Manning, C. E. Subducting carbon. *Nature* **574**, 343–352 (2019).

- 87. Kopp, R. E., Kirschvink, J. L., Hilburn, I. A. & Nash, C. Z. The Paleoproterozoic snowball Earth: A climate disaster triggered by the evolution of oxygenic photosynthesis. *Proceedings of the National Academy of Science* **102**, 11131–11136 (2005).
- 88. Bains, W., Petkowski, J. J., Rimmer, P. B. & Seager, S. Production of ammonia makes Venusian clouds habitable and explains observed cloud-level chemical anomalies. *Proceedings of the National Academy of Science* **118**, e2110889118 (2021). 2112.10850.
- 89. Jordan, S., Shorttle, O. & Rimmer, P. B. Proposed energy-metabolisms cannot explain the atmospheric chemistry of Venus. *Nature Communications* **13**, 3274 (2022). 2206.
- 90. McKay, C. P. & Smith, H. D. Possibilities for methanogenic life in liquid methane on the surface of Titan. *Icarus* **178**, 274–276 (2005).
- 91. McKay, C. P. Titan as the Abode of Life. *Life* **6**, 8 (2016).
- 92. Kharecha, P., Kasting, J. & Siefert, J. A coupled atmosphere-ecosystem model of the early Archean Earth. *Geobiology* **3**, 53–76 (2005).
- 93. Schwieterman, E. W. *et al.* Rethinking CO Antibiosignatures in the Search for Life Beyond the Solar System. *Astrophys. J.* **874**, 9 (2019). 1903.07661.
- 94. Sauterey, B., Charnay, B., Affholder, A., Mazevet, S. & Ferrière, R. Co-evolution of primitive methane-cycling ecosystems and early Earth's atmosphere and climate. *Nature Communications* **11**, 2705 (2020). 2006.06433.

- 95. Thompson, M. A., Krissansen-Totton, J., Wogan, N., Telus, M. & Fortney, J. J. The case and context for atmospheric methane as an exoplanet biosignature. *Proceedings of the National Academy of Science* **119**, e2117933119 (2022). 2204.04257.
- 96. Gao, P., Hu, R., Robinson, T. D., Li, C. & Yung, Y. L. Stability of CO2 Atmospheres on Desiccated M Dwarf Exoplanets. *Astrophys. J.* **806**, 249 (2015). 1501.06876.
- 97. Wogan, N. F. & Catling, D. C. When is Chemical Disequilibrium in Earth-like Planetary Atmospheres a Biosignature versus an Anti-biosignature? Disequilibria from Dead to Living Worlds. *Astrophys. J.* **892**, 127 (2020). 1911.06852.
- 98. Hoehler, T. M. Implications of H₂/CO₂ disequilibrium for life on Enceladus. *Nature*Astronomy 6, 3–4 (2022).
- 99. Diamond, L. W. & Akinfiev, N. N. Solubility of co2 in water from -1.5 to 100°c and from 0.1 to 100 mpa: evaluation of literature data and thermodynamic modelling. *Fluid Phase Equilibria* **208**, 265–290 (2003). URL https://www.sciencedirect.com/science/article/pii/S0378381203000414.
- 100. Mitchell, M. J., Jensen, O. E., Cliffe, K. A. & Maroto-Valer, M. M. A model of carbon dioxide dissolution and mineral carbonation kinetics. *Proceedings of the Royal Society of London Series A* **466**, 1265–1290 (2010).
- 101. Zeebe, R. E. History of seawater carbonate chemistry, atmospheric co2, and ocean acidification. *Annual Review of Earth and Planetary Sciences* **40**, 141–165 (2012). URL

- https://doi.org/10.1146/annurev-earth-042711-105521. https://doi.org/10.1146/annurev-earth-042711-105521.
- 102. Höning, D., Baumeister, P., Grenfell, J. L., Tosi, N. & Way, M. J. Early Habitability and Crustal Decarbonation of a Stagnant-Lid Venus. *Journal of Geophysical Research* (*Planets*) **126**, e06895 (2021). 2109.08756.
- 103. Tomkinson, T., Lee, M. R., Mark, D. F. & Smith, C. L. Sequestration of Martian CO₂ by mineral carbonation. *Nature Communications* **4**, 2662 (2013).
- 104. Steele, A. *et al.* Organic synthesis associated with serpentinization and carbonation on early Mars. *Science* **375**, 172–177 (2022).
- 105. Milliken, R. E. & Rivkin, A. S. Brucite and carbonate assemblages from altered olivinerich materials on Ceres. *Nature Geoscience* **2**, 258–261 (2009).
- 106. Graham, R. J. & Pierrehumbert, R. Thermodynamic and Energetic Limits on Continental Silicate Weathering Strongly Impact the Climate and Habitability of Wet, Rocky Worlds. Astrophys. J. 896, 115 (2020). 2004.14058.
- 107. Hakim, K. *et al.* Lithologic Controls on Silicate Weathering Regimes of Temperate Planets. *The Planetary Science Journal* **2**, 49 (2021). 2008.11620.
- 108. Wordsworth, R. D. & Pierrehumbert, R. T. Water Loss from Terrestrial Planets with CO₂-rich Atmospheres. *Astrophys. J.* **778**, 154 (2013). 1306.3266.

- 109. Klein, F. & Garrido, C. J. Thermodynamic constraints on mineral carbonation of serpentinized peridotite. *Lithos* **126**, 147–160 (2011).
- 110. Kelemen, P. B. & Matter, J. From the Cover: In situ carbonation of peridotite for CO2 storage. *Proceedings of the National Academy of Science* **105**, 17295–17300 (2008).
- 111. Way, M. J. et al. Was Venus the first habitable world of our solar system? Geophysics Research Letters 43, 8376–8383 (2016). 1608.00706.
- 112. Krissansen-Totton, J., Fortney, J. J. & Nimmo, F. Was Venus Ever Habitable? Constraints from a Coupled Interior-Atmosphere-Redox Evolution Model. *The Planetary Science Journal* 2, 216 (2021). 2111.00033.
- 113. Kasting, J. F., Pollack, J. B. & Ackerman, T. P. Response of Earth's atmosphere to increases in solar flux and implications for loss of water from Venus. *Icarus* **57**, 335–355 (1984).
- 114. Hamano, K., Abe, Y. & Genda, H. Emergence of two types of terrestrial planet on solidification of magma ocean. *Nature* **497**, 607–610 (2013).
- 115. Turbet, M. *et al.* Day-night cloud asymmetry prevents early oceans on Venus but not on Earth. *Nature* **598**, 276–280 (2021). 2110.08801.
- 116. Bean, J. L., Abbot, D. S. & Kempton, E. M. R. A Statistical Comparative Planetology Approach to the Hunt for Habitable Exoplanets and Life Beyond the Solar System. *Astrophys. J., Letters* **841**, L24 (2017). 1705.06288.

- 117. Turbet, M. Two examples of how to use observations of terrestrial planets orbiting in temperate orbits around low mass stars to test key concepts of planetary habitability. In Di Matteo, P. et al. (eds.) SF2A-2019: Proceedings of the Annual meeting of the French Society of Astronomy and Astrophysics, Di (2019).
- 118. Lehmer, O. R., Catling, D. C. & Krissansen-Totton, J. Carbonate-silicate cycle predictions of Earth-like planetary climates and testing the habitable zone concept. *Nature Communications* **11**, 6153 (2020). 2012.00819.
- 119. Lovelock, J. E. & Margulis, L. Atmospheric homeostasis by and for the biosphere: the gaia hypothesis. *Tellus* **26**, 2–10 (1974).
- 120. Lenton, T. Earth System Science: A Very Short Introduction (Oxford University Press, 2016). URL https://doi.org/10.1093/actrade/9780198718871.001.
- 121. Arthur, R. & Nicholson, A. A Gaian Habitable Zone. *arXiv e-prints* arXiv:2301.02150 (2023). 2301.02150.
- 122. Sagan, C. & Mullen, G. Earth and Mars: Evolution of Atmospheres and Surface Temperatures. *Science* **177**, 52–56 (1972).
- 123. Walker, J. C. G., Hays, P. B. & Kasting, J. F. A negative feedback mechanism for the long-term stabilization of the earth's surface temperature. *Journal of Geophysics Research* **86**, 9776–9782 (1981).

- 124. Arnscheidt, C. W. & H., R. D. Presence or absence of stabilizing earth system feedbacks on different time scales. *Science Advances* **8**, eadc9241 (2022). URL https://www.science.org/doi/abs/10.1126/sciadv.adc9241. https://www.science.org/doi/pdf/10.1126/sciadv.adc9241.
- 125. Weiss, L. M. *et al.* The California-Kepler Survey. V. Peas in a Pod: Planets in a Kepler Multi-planet System Are Similar in Size and Regularly Spaced. *Astron. J.* **155**, 48 (2018). 1706.06204.
- 126. Sandford, E., Kipping, D. & Collins, M. On planetary systems as ordered sequences.

 Mon. Not. R. Astron. Soc. 505, 2224–2246 (2021). 2105.09966.
- 127. Mishra, L. *et al.* The New Generation Planetary Population Synthesis (NGPPS) VI. Introducing KOBE: Kepler Observes Bern Exoplanets. Theoretical perspectives on the architecture of planetary systems: Peas in a pod. *Astron. Astrophys.* **656**, A74 (2021). 2105.12745.
- 128. Millholland, S. C. & Winn, J. N. Split Peas in a Pod: Intra-system Uniformity of Super-Earths and Sub-Neptunes. *Astrophys. J., Letters* **920**, L34 (2021). 2110.01466.
- 129. Goyal, A. V. & Wang, S. Generalized Peas in a Pod: Extending Intra-system Mass Uniformity to Non-TTV Systems via the Gini Index. *Astrophys. J.* **933**, 162 (2022). 2206.00053.

- 130. Snellen, I. *et al.* Combining high-dispersion spectroscopy with high contrast imaging: Probing rocky planets around our nearest neighbors. *Astron. Astrophys.* **576**, A59 (2015). 1503.01136.
- 131. Dressing, C. D. & Charbonneau, D. The Occurrence of Potentially Habitable Planets Orbiting M Dwarfs Estimated from the Full Kepler Dataset and an Empirical Measurement of the Detection Sensitivity. *Astrophys. J.* **807**, 45 (2015). 1501.01623.
- 132. Gaidos, E., Mann, A. W., Kraus, A. L. & Ireland, M. They are small worlds after all: revised properties of Kepler M dwarf stars and their planets. *Mon. Not. R. Astron. Soc.*457, 2877–2899 (2016). 1512.04437.
- 133. Hinkel, N. R., Timmes, F. X., Young, P. A., Pagano, M. D. & Turnbull, M. C. Stellar Abundances in the Solar Neighborhood: The Hypatia Catalog. *Astron. J.* **148**, 54 (2014). 1405.6719.
- 134. Putirka, K. D. & Rarick, J. C. The composition and mineralogy of rocky exoplanets: A survey of ¿4000 stars from the Hypatia Catalog. *American Mineralogist* **104**, 817–829 (2019). 1907.05506.
- 135. Gordon, I. et al. The hitran2020 molecular spectroscopic database. *Journal of Quantitative Spectroscopy and Radiative Transfer* **277**, 107949 (2022).
- 136. Gressier, A. *et al.* Near-infrared transmission spectrum of TRAPPIST-1 h using Hubble WFC3 G141 observations. *Astron. Astrophys.* **658**, A133 (2022). 2112.05510.

- 137. Turbet, M. *et al.* A Review of Possible Planetary Atmospheres in the TRAPPIST-1 System. *Space Science Reviews* **216**, 100 (2020). 2007.03334.
- 138. Agol, E. *et al.* Refining the Transit-timing and Photometric Analysis of TRAPPIST-1: Masses, Radii, Densities, Dynamics, and Ephemerides. *The Planetary Science Journal* 2, 1 (2021). 2010.01074.
- 139. Rackham, B. *et al.* ACCESS I: An Optical Transmission Spectrum of GJ 1214b Reveals a Heterogeneous Stellar Photosphere. *Astrophys. J.* **834**, 151 (2017). 1612.00228.
- 140. Rackham, B. V., Apai, D. & Giampapa, M. S. The Transit Light Source Effect: False Spectral Features and Incorrect Densities for M-dwarf Transiting Planets. *Astrophys. J.* 853, 122 (2018). 1711.05691.
- 141. Komacek, T. D., Fauchez, T. J., Wolf, E. T. & Abbot, D. S. Clouds will Likely Prevent the Detection of Water Vapor in JWST Transmission Spectra of Terrestrial Exoplanets.

 *Astrophys. J., Letters 888, L20 (2020). 1912.08781.
- 142. May, E. M., Taylor, J., Komacek, T. D., Line, M. R. & Parmentier, V. Water Ice Cloud Variability and Multi-epoch Transmission Spectra of TRAPPIST-1e. *Astrophys. J., Letters* 911, L30 (2021). 2103.09313.
- 143. Stevenson, K. *et al.* Tell Me How I?m Supposed To Breathe With No Air: Measuring the Prevalence and Diversity of M-Dwarf Planet Atmospheres. JWST Proposal. Cycle 1, ID. #1981 (2021).

- 144. Niraula, P. *et al.* The impending opacity challenge in exoplanet atmospheric characterization. *Nature Astronomy* **6**, 1287–1295 (2022). 2209.07464.
- 145. Mollière, P. *et al.* petitRADTRANS. A Python radiative transfer package for exoplanet characterization and retrieval. *Astron. Astrophys.* **627**, A67 (2019). 1904.11504.
- 146. Line, M. R. *et al.* A solar C/O and sub-solar metallicity in a hot Jupiter atmosphere.

 *Nature 598, 580–584 (2021). 2110.14821.
- 147. Farquhar, G. D., Ehleringer, J. R. & Hubick, K. T. Carbon isotope discrimination and photosynthesis. *Annual Review of Plant Physiology and Plant Molecular Biology* 40, 503–537 (1989). URL https://doi.org/10.1146/annurev.pp.40.060189.002443.
 https://doi.org/10.1146/annurev.pp.40.060189.002443.
- 148. Estep, M. F. & Hoering, T. C. Biogeochemistry of the stable hydrogen isotopes. *Geochimica Cosmochimica Acta* **44**, 1197–1206 (1980).
- 149. Woods, P. M. Carbon isotope measurements in the Solar System. *arXiv e-prints* arXiv:0901.4513 (2009). 0901.4513.
- 150. Schidlowski, M. Carbon isotopes as biogeochemical recorders of life over 3.8 Ga of Earth history: evolution of a concept. *Precambrian Research* **106**, 117–134 (2001).
- 151. Krissansen-Totton, J., Buick, R. & Catling, D. C. A statistical analysis of the carbon isotope record from the Archean to Phanerozoic and implications for the rise of oxygen.

 *American Journal of Science 315, 275–316 (2015).

- 152. Garcia, A. K., Cavanaugh, C. M. & Kacar, B. The curious consistency of carbon biosignatures over billions of years of Earth-life coevolution. *The ISME Journal* **15**, 2183–2194 (2021).
- 153. Jakosky, B. M. *et al.* Mars' atmospheric history derived from upper-atmosphere measurements of ¡sup¿38¡/sup¿ar/¡sup¿36¡/sup¿ar. *Science* **355**, 1408–1410 (2017).

 URL https://www.science.org/doi/abs/10.1126/science.aai7721.

 https://www.science.org/doi/pdf/10.1126/science.aai7721.
- 154. Jakosky, B. M. *et al.* Loss of the Martian atmosphere to space: Present-day loss rates determined from MAVEN observations and integrated loss through time. *Icarus* **315**, 146–157 (2018).
- 155. Glidden, A., Seager, S., Huang, J., Petkowski, J. J. & Ranjan, S. Can Carbon Fractionation Provide Evidence for Aerial Biospheres in the Atmospheres of Temperate Sub-Neptunes?

 Astrophys. J. 930, 62 (2022). 2205.06284.
- 156. Ratner, M. I. & Walker, J. C. Atmospheric ozone and the history of life. *Journal of Atmospheric Sciences* **29**, 803–808 (1972).
- 157. Kasting, J. F. & Donahue, T. M. The evolution of atmospheric ozone. *Journal of Geo- physics Research* **85**, 3255–3263 (1980).
- 158. Leger, A., Pirre, M. & Marceau, F. J. Search for primitive life on a distant planet: relevance of 02 and 03 detections. *Astron. Astrophys.* **277**, 309 (1993).

- 159. Barstow, J. K. & Irwin, P. G. J. Habitable worlds with JWST: transit spectroscopy of the TRAPPIST-1 system? *Mon. Not. R. Astron. Soc.* **461**, L92–L96 (2016). 1605.07352.
- 160. Wang, F., Dreisinger, D., Jarvis, M. & Hitchins, T. Kinetics and mechanism of mineral carbonation of olivine for co2 sequestration. *Minerals Engineering* **131**, 185–197 (2019). URL https://www.sciencedirect.com/science/article/pii/S0892687518305077.
- 161. Kelemen, P. B. *et al.* Engineered carbon mineralization in ultramafic rocks for co2 removal from air: Review and new insights. *Chemical Geology* **550**, 119628 (2020). URL https://www.sciencedirect.com/science/article/pii/S0009254120301674.
- 162. Loring, J. S. et al. In Situ Infrared Spectroscopic Study of Brucite Carbonation in Dry to Water-Saturated Supercritical Carbon Dioxide. *Journal of Physical Chemistry A* 116, 4768–4777 (2012).
- 163. Heng, K. & Kopparla, P. On the Stability of Super-Earth Atmospheres. *Astrophys. J.* **754**, 60 (2012). 1203.1922.
- 164. Turbet, M. *et al.* Modeling climate diversity, tidal dynamics and the fate of volatiles on TRAPPIST-1 planets. *Astron. Astrophys.* **612**, A86 (2018). 1707.06927.
- 165. Selsis, F., Despois, D. & Parisot, J. P. Signature of life on exoplanets: Can Darwin produce false positive detections? *Astron. Astrophys.* **388**, 985–1003 (2002).

- 166. James, T. & Hu, R. Photochemical Oxygen in Non-1-bar CO₂ Atmospheres of Terrestrial Exoplanets. *Astrophys. J.* **867**, 17 (2018). 1809.04545.
- 167. Kopparapu, R. k. *et al.* Habitable Moist Atmospheres on Terrestrial Planets near the Inner Edge of the Habitable Zone around M Dwarfs. *Astrophys. J.* **845**, 5 (2017). 1705. 10362.
- 168. Afrin Badhan, M. *et al.* Stellar Activity Effects on Moist Habitable Terrestrial Atmospheres around M Dwarfs. *Astrophys. J.* **887**, 34 (2019). 1902.04086.
- 169. Segura, A. *et al.* Biosignatures from Earth-Like Planets Around M Dwarfs. *Astrobiology* 5, 706–725 (2005). astro-ph/0510224.
- 170. Rugheimer, S., Kaltenegger, L., Segura, A., Linsky, J. & Mohanty, S. Effect of UV Radiation on the Spectral Fingerprints of Earth-like Planets Orbiting M Stars. *Astrophys. J.* **809**, 57 (2015). 1506.07202.
- 171. Liggins, P., Jordan, S., Rimmer, P. B. & Shorttle, O. Growth and Evolution of Secondary Volcanic Atmospheres: I. Identifying the Geological Character of Hot Rocky Planets. *Journal of Geophysical Research (Planets)* 127, e07123 (2022). 2111.05161.
- 172. Lichtenberg, T., Schaefer, L. K., Nakajima, M. & Fischer, R. A. Geophysical Evolution During Rocky Planet Formation. *arXiv e-prints* arXiv:2203.10023 (2022). 2203. 10023.

- 173. Wordsworth, R. D., Schaefer, L. K. & Fischer, R. A. Redox Evolution via Gravitational Differentiation on Low-mass Planets: Implications for Abiotic Oxygen, Water Loss, and Habitability. *Astron. J.* **155**, 195 (2018). 1710.00345.
- 174. Ormel, C. W., Liu, B. & Schoonenberg, D. Formation of TRAPPIST-1 and other compact systems. *Astron. Astrophys.* **604**, A1 (2017). 1703.06924.
- 175. Bitsch, B., Raymond, S. N. & Izidoro, A. Rocky super-Earths or waterworlds: the interplay of planet migration, pebble accretion, and disc evolution. *Astron. Astrophys.* **624**, A109 (2019). 1903.02488.
- 176. Venturini, J., Guilera, O. M., Haldemann, J., Ronco, M. P. & Mordasini, C. The nature of the radius valley. Hints from formation and evolution models. *Astron. Astrophys.* **643**, L1 (2020). 2008.05513.
- 177. Ortenzi, G. *et al.* Mantle redox state drives outgassing chemistry and atmospheric composition of rocky planets. *Scientific Reports* **10**, 10907 (2020).
- 178. Bower, D. J., Hakim, K., Sossi, P. A. & Sanan, P. Retention of Water in Terrestrial Magma Oceans and Carbon-rich Early Atmospheres. *The Planetary Science Journal* 3, 93 (2022). 2110.08029.
- 179. Aschenbrenner, O. & Styring, P. Comparative study of solvent properties for carbon dioxide absorption. *Energy Environ. Sci.* **3**, 1106–1113 (2010). URL http://dx.doi.org/10.1039/C002915G.

- 180. Dalmolin, I. *et al.* Solubility of carbon dioxide in binary and ternary mixtures with ethanol and water. *Fluid Phase Equilibria* **245**, 193–200 (2006). URL https://www.sciencedirect.com/science/article/pii/S0378381206002020.
- 181. Fogg, P. Preface. In FOGG, P. G. (ed.) *Carbon Dioxide in Non-Aqueous Solvents At Pressures Less Than 200 KPA*, IUPAC Solubility Data Series, ix (Pergamon, Amsterdam, 1992). URL https://www.sciencedirect.com/science/article/pii/B97800804049505000051.
- 182. Wolszczan, A. & Frail, D. A. A planetary system around the millisecond pulsar PSR1257 + 12. *Nature* **355**, 145–147 (1992).
- 183. Mayor, M. & Queloz, D. A Jupiter-mass companion to a solar-type star. *Nature* **378**, 355–359 (1995).
- 184. Lovis, C. *et al.* An extrasolar planetary system with three Neptune-mass planets. *Nature*441, 305–309 (2006). astro-ph/0703024.
- 185. Doyle, L. R. *et al.* Kepler-16: A Transiting Circumbinary Planet. *Science* **333**, 1602 (2011). 1109.3432.
- 186. Reynolds, R. T., Squyres, S. W., Colburn, D. S. & McKay, C. P. On the habitability of Europa. *Icarus* **56**, 246–254 (1983).
- 187. Vance, S. D. *et al.* Geophysical Investigations of Habitability in Ice-Covered Ocean Worlds. *Journal of Geophysical Research (Planets)* **123**, 180–205 (2018). 1705.03999.

- 188. Southam, G., Westall, F. & Spohn, T. Geology, Life, and Habitability. In Schubert, G. (ed.) *Treatise on Geophysics*, 473–486 (2015).
- 189. Kitzmann, D. *et al.* The unstable CO₂ feedback cycle on ocean planets. *Mon. Not. R. Astron. Soc.* **452**, 3752–3758 (2015). 1507.01727.
- 190. Graham, R. J., Lichtenberg, T. & Pierrehumbert, R. T. CO₂ Ocean Bistability on Terrestrial Exoplanets. *Journal of Geophysical Research (Planets)* **127**, e2022JE007456 (2022). 2210.00149.
- 191. Bercovici, D. & Ricard, Y. Energetics of a two-phase model of lithospheric damage, shear localization and plate-boundary formation. *Geophysical Journal International* **152**, 581–596 (2003).
- 192. Korenaga, J. Initiation and Evolution of Plate Tectonics on Earth: Theories and Observations. *Annual Review of Earth and Planetary Sciences* **41**, 117–151 (2013).
- 193. Mei, S. & Kohlstedt, D. L. Influence of water on plastic deformation of olivine aggregates:
 2. Dislocation creep regime. *Journal of Geophysics Research* 105, 21,471–21,481 (2000).
- 194. Mei, S. & Kohlstedt, D. L. Influence of water on plastic deformation of olivine aggregates:

 1. Diffusion creep regime. *Journal of Geophysics Research* **105**, 21,457–21,469 (2000).
- 195. Zanazzi, J. J. & Triaud, A. H. M. J. The ability of significant tidal stress to initiate plate tectonics. *Icarus* **325**, 55–66 (2019).

- 196. Kral, Q. *et al.* Cometary impactors on the TRAPPIST-1 planets can destroy all planetary atmospheres and rebuild secondary atmospheres on planets f, g, and h. *Mon. Not. R. Astron. Soc.* **479**, 2649–2672 (2018). 1802.05034.
- 197. Borgeat, X. & Tackley, P. J. Hadean/Eoarchean tectonics and mantle mixing induced by impacts: a three-dimensional study. *Progress in Earth and Planetary Science* **9**, 38 (2022).
- 198. Greaves, J. S. et al. Phosphine gas in the cloud decks of Venus. Nature Astronomy 5, 655–664 (2021). 2009.06593.
- 199. Krasnopolsky, V. A., Maillard, J. P. & Owen, T. C. Detection of methane in the martian atmosphere: evidence for life? *Icarus* **172**, 537–547 (2004).
- 200. Kargel, J. S. *et al.* Europa's Crust and Ocean: Origin, Composition, and the Prospects for Life. *Icarus* **148**, 226–265 (2000).
- 201. McKay, C. P., Porco Carolyn C., Altheide, T., Davis, W. L. & Kral, T. A. The Possible Origin and Persistence of Life on Enceladus and Detection of Biomarkers in the Plume.
 Astrobiology 8, 909–919 (2008).
- 202. Batalha, N. E. & Line, M. R. Information Content Analysis for Selection of Optimal JWST Observing Modes for Transiting Exoplanet Atmospheres. *Astron. J.* 153, 151 (2017). 1612.02085.

- 203. Witte, S., Helling, C., Barman, T., Heidrich, N. & Hauschildt, P. H. Dust in brown dwarfs and extra-solar planets. III. Testing synthetic spectra on observations. *Astron. Astrophys.* **529**, A44 (2011).
- 204. Rackham, B. V. speclib (2023). URL https://doi.org/10.5281/zenodo. 7868050.