

Atmospheric Biosignatures
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Abstract

Life has likely coevolved with the Earth system in time in various ways. Our oxygen-rich atmosphere and the protective ozone layer are mainly the result of photosynthetic activity. Additionally, bacteria emit greenhouse gases such as methane and nitrous oxide into the atmosphere, and vegetation can emit a variety of organic molecules. In an exoplanetary context, it is important to consider whether such gas-phase species – so-called atmospheric biosignatures – could be detected spectroscopically and attributed to extraterrestrial life. Another signature of life on Earth is the so-called redox disequilibrium of its atmosphere. This refers to the presence of simultaneously oxidizing and reducing species (e.g., molecular oxygen and methane). Without life, such species would react and

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be removed on relatively fast timescales. Since Earth's atmosphere has changed considerably during its history, we will also consider atmospheric biosignatures in the context of the early Earth. This chapter will present a brief literature review of atmospheric biosignatures. We will discuss the main photochemical responses of such species in the modern and early Earth's atmosphere and their potential to act as atmospheric biosignatures in an exoplanetary context.

Introduction

Life has likely coevolved intricately with the Earth system over our planet's history. This chapter presents a brief review of atmospheric exoplanetary biosignatures, including their chemical and physical responses and spectrophotometric detectability. A common approach when estimating atmospheric exoplanetary signals is to apply numerical models of Earth-like planets and/or to extrapolate what has been learned from observational and modeling studies of these species on the (early) Earth, on Solar System objects, and on Earth-like exoplanets. Also discussed in the context of exoplanetary biosignatures is the concept of redox disequilibrium and so-called dead Earths which are simulated in order to provide a benchmark to compare against when assessing atmospheric biosignatures. The chapter is divided according to atmospheric species which are commonly discussed in an exoplanet context. For a broad introduction to the subject, the interested reader is referred to, e.g., Seager et al. [\(2013,](#page-12-0) [2016\)](#page-12-1), Meadows et al. [\(2017\)](#page-11-0), Grenfell [\(2017\)](#page-10-0), and the five review articles from the NASA Nexus for Exoplanet System Science (NExSS) Exoplanet Biosignatures Workshop Without Walls, Schwieterman et al. [\(2018,](#page-12-2) in press), Meadows et al. [\(2018,](#page-11-1) in press), Catling et al. [\(2018,](#page-9-2) in press), Walker et al. [\(2017\)](#page-12-3), and Fujii et al. [\(2017\)](#page-10-1). Our chapter finishes with some brief conclusions and recommendations.

Oxygen (O₂)

Modern Earth – O_2 is a rather inert atmospheric species which maintains a constant volume mixing ratio (vmr) (=0.21) in modern Earth's atmosphere up to \sim 80 km altitude (Brasseur and Solomon [2006\)](#page-9-3). At higher atmospheric levels, it is photolyzed and can be re-formed to generate the "oxygen airglow," a feature also detected in the atmospheres of Mars and Venus (see Slanger and Copeland [2003;](#page-12-4) Crisp et al. [1996;](#page-10-2) Allen et al. [1992\)](#page-9-4). The major source of atmospheric O_2 on the modern Earth is photosynthesis coupled with burial of organic material into the Earth's mantle (Holland [2006\)](#page-10-3). A weaker source on modern Earth involves breakdown of water followed by escape of the resulting H-atoms. The main sinks involve reaction with reduced volcanic gases (Catling and Claire [2005\)](#page-9-5) and surface weathering (e.g., Holland [2002\)](#page-10-4). Model studies of the O_2 global budget include, e.g., Holland [\(1984\)](#page-10-5), Kump [\(1988\)](#page-11-2), Van Capellen and Ingall [\(1996\)](#page-12-5), Lenton and Watson [\(2000\)](#page-11-3), Berner et al. [\(2000\)](#page-9-6), and Berner [\(2001\)](#page-9-7).

Early Earth – the early Earth's atmosphere was strongly reducing and low in $O₂$ during the Archaean period. An initial rise in $O₂$ termed the "Great Oxidation" Event" (GOE) took place ${\sim}2.5$ Gyr ago at the end of the Archaean followed by a smaller, second rise – the "Second Oxidation Event" (SOE) \sim 0.6 Gyr ago. Possible explanations for the GOE include, e.g., a faster burial rate (Kump et al. [2011\)](#page-11-4) or less-reducing volcanic emissions (Gaillard et al. [2011\)](#page-10-6). Gebauer et al. [\(2017\)](#page-10-7) investigated chemical pathways affecting $O₂$ on the early Earth and suggested complex oxidation pathways which remove $O₂$ in the lower atmosphere with via, e.g., $CO₂$ photolysis forming $O₂$ at higher atmospheric levels.

Solar System – Mars and Venus have $CO₂$ -dominated atmospheres which can form small amounts of O_2 abiotically via photolysis (see, e.g., Yung and DeMore [1999](#page-13-0) and references therein) although the amount formed is much smaller than the biotically produced O_2 on Earth. Catalytic cycles involving, e.g., hydrogen or nitrogen oxides control the regeneration of CO back into $CO₂$. Abiotic production of O_2 is also important to consider in the context of exoplanets O_2 (see below). Clearly, it is critical to understand all potential abiotic sources of proposed biosignatures in order to rule out so-called false positives, i.e., a false detection of life.

Earth-Like Exoplanets – whether or not the oxygen cycle plays a role on Earthlike planets is not well-constrained, although some preliminary theoretical studies have been performed. For instance, Kiang et al. [\(2007\)](#page-10-8) investigated theoretical constraints for photosynthesis on Earth-like worlds orbiting different types of stars. Release of photosynthetically generated oxygen into Earth's atmosphere is related to the rate of burial of organic material. Burial proceeds faster around continental shelfs so is likely linked with the distribution of continents. Burial and subduction are however linked by plate tectonics, the efficiency of which on Earth-like planets and super-Earths is much debated (see, e.g., Noack and Breuer 2014). The $O₂$ source due to H-escape (mentioned above) could be highly efficient for low-mass planets in high EUV environments (e.g., for planets orbiting pre-main sequence and early post-main sequence stars). In a separate chapter of this book, Harman and Domagal-Goldman discuss abiotic O_2 sources relevant to exoplanetary biosignature assessment. Regarding potential sinks of oxygen, some model studies (e.g., Segura et al. [2003,](#page-12-6) [2005\)](#page-12-7) have calculated that CH_4 (an O_2 sink) may be up to 1000 times more abundant in the atmospheres of Earth-like planets orbiting M-dwarf stars compared to modern Earth. This is because weaker UV output from the star leads to lower OH production, which is the main sink for CH4. Regarding the evolution of O_2 signals over time, Kaltenegger et al. [\(2007\)](#page-10-9) suggested that detectable features could become apparent after \sim 2Gyr assuming a similar evolution as the Earth.

Spectral Detectability – O_2 possesses rather narrow absorption features, e.g., the "A Band" in the visible region at $0.76 \mu m$ (as discussed in, e.g., Des Marais et al. 2002). Additional features are the "B Band" at 0.68 μ m and near-infrared features near 1.3μ m. Various theoretical studies have investigated the potential for next-generation instruments to detect O_2 in Earth-like planetary atmospheres (Rodler and López-Morales [2014;](#page-12-8) Kawahara et al. [2012;](#page-10-11) Misra et al. [2014;](#page-11-6) Snellen [2014\)](#page-12-9).

Ozone (O3)

Modern Earth Stratosphere – the ozone layer on modern Earth extends from about 20–50 km with maximum O_3 mixing ratios of \sim 10 parts per million (ppm) occurring around 30 km in the mid-stratosphere. Sydney Chapman first accounted for the existence of the ozone layer (Chapman [1930\)](#page-9-8) by proposing the so-called Chapman mechanism. The mechanism involves a series of gas-phase reactions involving chemical species which contain only oxygen. It was originally formulated to explain the location and magnitude of Earth's ozone layer by presenting chemical reactions which lead to ozone formation and loss. The mechanism first involves photolysis of molecular oxygen into two oxygen atoms, one of which can combine with O_2 to form O_3 . Stratospheric O_3 on Earth is thereby mainly formed from photolysis of O_2 in the presence of UV of the appropriate wavelengths (see, e.g., Brasseur and Solomon [2006\)](#page-9-3). Since it is mainly formed from atmospheric O_2 , O_3 can be considered a type of biosignature under certain conditions. $O₃$ is destroyed by certain families of gases (e.g., $HOx = OH + HO₂$); family members (e.g., OH, $HO₂$) quickly interchange depending on, e.g., p, T, and insolation. O₃-destroying families include HOx (in the stratosphere and mesosphere; Bates and Nicolet [1950\)](#page-9-9), ClOx (mostly in the upper stratosphere; Stolarski and Cicerone [1974\)](#page-12-10), and NOx (peaking in the lower stratosphere; Crutzen [1970\)](#page-10-12). HOx, NOx, and ClOx participate in catalytic cycles which efficiently remove $O_3(g)$ (see, e.g., Wayne [1993\)](#page-12-11). An important general cycle is:

$$
X + O_3 \rightarrow XO + O_2
$$

$$
XO + O \rightarrow X + O_2
$$

$$

$$

net :
$$
O_3 + O \rightarrow O_2 + O_2
$$

where $X = (e.g., CI, OH, NO)$. So-called "storage" or "reservoir" species (e.g., $HNO₃$ "store," e.g., the families (HOx, NOx, ClOx, etc.) in inactive forms and can release them depending on conditions of, e.g., UV or temperature.

Ozone has a chemical lifetime of a few weeks in the lower stratosphere where its abundance is mainly affected by transport ("dynamically controlled"). In the upper stratosphere, it has a lifetime of minutes to hours and is therefore mainly affected by chemistry ("photochemically controlled") (World Meteorological Organization Report [1995\)](#page-13-1). The main source of ozone at lower latitudes is the Chapman mechanism. Ozone formed in the tropics is then transported to higher latitudes via the Brewer-Dobson circulation in the middle atmosphere. Ozone is a radiatively active gas, which efficiently shields the planetary surface by absorbing harmful UV, which in turn causes stratospheric heating.

Modern Earth Troposphere – weaker UV in the lower atmosphere leads to a slowing in the Chapman mechanism. An alternative mechanism, sometimes called the "smog mechanism" is mainly responsible for lower atmosphere ozone production (Haagen-Smit [1952\)](#page-10-13). This process requires organic molecules (such as CH4) in the presence of UV and is catalyzed by NOx. On Earth this mechanism can be driven by either the abundance of atmospheric organic molecules or NOx depending on environmental conditions (T, p, UV). The smog (tropospheric) component on Earth typically constitutes ${\sim}10\%$ of the total overhead ozone column.

Early Earth – formation of Earth's ozone layer from atmospheric oxygen is generally acknowledged to proceed quickly compared with Earth's oxygenation timescale, so the modern ozone layer probably formed (at least 90% of the ozone column) at or around the time of the GOE (Kasting and Catling [2003;](#page-10-14) Segura et al. [2003;](#page-12-6) Gebauer et al. [2017\)](#page-10-7).

Solar System – CO_2 photolysis (see above) can produce O_2 and hence O_3 abiotically. Low amounts of O_3 have indeed been found in the CO_2 -dominated atmospheres of Venus (Montmessin et al. [2011\)](#page-11-7) and Mars (e.g., Perrier et al. [2006\)](#page-11-8).

Earth-Like Exoplanets – a key issue is to estimate the response of atmospheric biosignatures such as ozone over the wide range of planetary parameters relevant in Earth-like exoplanet science. Numerous studies (e.g., Segura et al. [2003,](#page-12-6) [2005;](#page-12-7) Tinetti et al. [2006;](#page-12-12) Grenfell et al. [2007;](#page-10-15) Rauer et al. [2011;](#page-11-9) Hedelt et al. [2013;](#page-10-16) Rugheimer et al. [2015\)](#page-12-13) assume Earth's evolution, size, etc. and then apply numerical models to investigate the effect of changing key planetary input parameters such as the incoming insolation from the central star, the orbit parameters, the biomass emitted from the surface emissions, etc. Earth-like planets orbiting M-dwarf stars are in particular key objects of study being favored targets – although the effect of potentially strong bombardment of the planetary atmosphere by cosmic rays and flares upon atmospheric biosignatures such as ozone is potentially significant (see, e.g., Segura et al. [2010;](#page-12-14) Grenfell et al. [2012;](#page-10-17) Tabataba-Vakili et al. [2016\)](#page-12-15).

Earth-Like Exoplanets' Evolution in Time – a cornerstone study by Des Marais et al. [\(2002\)](#page-10-10) discussed atmospheric ozone spectral features in emission and reflection for stratospheric abundances varying from 0 to 6 parts per million. Several studies, e.g., Segura et al. [\(2003\)](#page-12-6) and Kaltenegger et al. [\(2007\)](#page-10-9), investigated the development of ozone spectral features assuming an Earth-like planetary evolution.

Spectral Detectability – Ozone's main spectral feature occurs at $9.6 \mu m$ in the infrared. Ozone features are also strongly apparent in the visible and UV: Earth's spectrum features the broad Chappuis band from $(0.5-0.7)$ μ m, and the Hartley band produces an abrupt spectral falloff in the Earth's spectrum shortward of $0.3 \mu m$. Band strength in the IR is rather sensitive to the temperature difference between the lower and middle atmosphere, which in turn could be sensitive to the central star (see, e.g., Rauer et al. [2011](#page-11-9) for a discussion). Detecting and retrieving ozone (see discussions in von Paris et al. [2013;](#page-12-16) Hedelt et al. [2013\)](#page-10-16) may be very challenging on Earth-like planets using the James Webb Space Telescope (JWST): Barstow et al. [\(2016\)](#page-9-10) concluded that 30 transits would be required by JWST to detect Earth's ozone layer for the exoplanets TRAPPIST-1c and TRAPPIST-1d (assuming an Earth twin, although these planets are much hotter than Earth). There is furthermore potential overlap in the IR of O_3 and CO_2 spectral bands (Selsis et al. [2002;](#page-12-17) von Paris et al. [2011\)](#page-12-18), weakening of ozone spectral features by clouds (Kitzmann et al. [2011\)](#page-11-10), and possible interferences due to the presence of a moon (Robinson et al. [2011\)](#page-12-19).

Nitrous Oxide (N2O)

Modern Earth – N_2O in modern Earth's atmosphere has a surface abundance of 3.3×10^{-7} vmr (IPCC [2007\)](#page-10-18), and since its global inventory is strongly affected by biological activity (e.g., Bouwman et al. [1995\)](#page-9-11), it has been studied in the exoplanetary literature as a biosignature candidate (see, e.g., Segura et al. [2003\)](#page-12-6). On modern Earth, known abiotic sources of N_2O are \sim 2 orders of magnitude lower (Kaiser and Röckmann [2005;](#page-10-19) Samarkin et al. [\(2010\)](#page-12-20)) than the biological sources. N2O is destroyed in the atmosphere (e.g., McElroy and McConnell [1971\)](#page-11-11) via UV photolysis and reactions with electronically excited oxygen atoms. Syakila and Kroeze [\(2011\)](#page-12-21) review N_2O global atmospheric sources and sinks on the modern Earth. $N₂O$ is a strong greenhouse gas due to several absorption bands across the thermal infrared, and it has a long chemical lifetime in the atmosphere of several hundred Earth years (IPCC [2007\)](#page-10-18).

Early Earth – model studies (Grenfell et al. [2011;](#page-10-20) Roberson et al. [2011\)](#page-12-22) have implied that N_2O could have played a role in warming the early Earth. Due to a potentially incomplete biological nitrogen cycle in the Proterozoic, Buick [\(2007\)](#page-9-12) suggested that this species could have accumulated in Earth's atmosphere and played an important role as a Proterozoic greenhouse gas. Mvondo et al. [\(2001\)](#page-11-12) suggested that N_2O could have built up on the early Earth due to lightning and corona discharge. More recently, Airapetian et al. [\(2016\)](#page-9-13) proposed that high-energy particles emitted by the young Sun could have induced $N₂O$ formation in early Earth's upper atmosphere, albeit at low abundance.

Solar System – production of N_2O in the atmospheres of early Venus and early Mars due to corona discharge has been proposed (Mvondo et al. [2001;](#page-11-12) Summers and Khare [2007\)](#page-12-23). Lightning is also a potential source for N_2O on Venus (e.g., Levine et al. [1979\)](#page-11-13).

Earth-Like Exoplanets – model studies (Segura et al. [2005;](#page-12-7) Grenfell et al. [2014;](#page-10-21) Rugheimer et al. [2015\)](#page-12-13) suggest that low-UV environments around quiescent Mdwarfs can cause buildup of N_2O due to decreased N_2O loss via firstly photolysis and secondly via reaction with $O(^1D)$. Similarly, N₂O can also be sensitive to the atmospheric O_3 abundance, which can modulate the UV reaching the planet's surface.

Earth-Like Exoplanets in Time – Airapetian et al. [\(2016\)](#page-9-13) suggested some $N_2O(g)$ production in N_2-O_2 atmospheres associated with, e.g., high-energy particles emitted by the central star. Although on the one hand the cosmic rays could break $N_2(g)$ and lead to N_2O production via their mechanism, the high UV would, on the other hand, favor N_2O destruction via photolysis (Segura et al. [2005\)](#page-12-7) – these processes require further investigation, e.g., over a wider range of flaring energies.

Spectral Detectability – N_2O produces rather weak spectral features for modern Earth conditions at 7.8, 4.5, and 3.7 μ m (Muller [2013\)](#page-11-14) which have some overlaps with CH_4 and H_2O bands. These features could become more significant for planets in weak-UV environments, where N_2O builds up, as discussed (e.g., Segura et al. [2005\)](#page-12-7). Grenfell et al. (2014) suggested that N₂O spectral bands could become more significant for Earth-like planets with reduced atmospheric $CH₄$ abundances (Grenfell et al. 2014) associated with stratospheric cooling (since CH_4 absorbs SW radiation and heats the middle atmosphere).

Methane (CH₄)

Modern Earth – features a CH₄ surface concentration of $\sim 1.8 \times 10^{-6}$ vmr. This corresponds to a net (=[natural+anthropogenic]) surface source of \sim 500Tg/year which is mainly $(\sim]90\%)$ associated with the respiration of methanogenic bacteria. Minor sources come from geological processes (Bousquet et al. [2006;](#page-9-14) Etiope and Sherwood Lollar [2013\)](#page-10-22). CH₄ is mainly destroyed in Earth's atmosphere via reaction with the hydroxyl (OH) radical. Secondary sinks arise due to, e.g., dry deposition, photolysis, and gas-phase reactions with species such as Cl. $CH₄$ is rather unreactive in the troposphere, featuring a lifetime against loss of \sim 8 years (IPCC, [2007\)](#page-10-18). It is therefore a tracer of dynamical motions in the lower atmosphere.

Early Earth – CH₄ may have been 500 times more abundant (up to \sim 1000 ppm) during the Archaean compared to today (\sim 1.8 ppmv) (Catling et al. [2001\)](#page-9-15). This high abundance likely arose from methanogenic production under a reducing atmosphere that increased the atmospheric lifetime of methane. It may also have been due to enhanced CH_4 emissions from volcanic activity (Kasting and Catling [2003\)](#page-10-14). Enhanced greenhouse warming from high CH4 on the early Earth has been proposed as a possible solution to the faint young Sun paradox (see, e.g., Catling et al. [2001\)](#page-9-15). High CH4 abundances in the Archean have also been postulated to have generated an intermittent organic haze, similar to that on Titan (e.g., Trainer et al. [2004;](#page-12-24) Zerkle et al. [2012\)](#page-13-2).

Solar System – Formisano et al. [\(2004\)](#page-10-23) claimed detection of atmospheric CH₄ of 10 ± 5 ppbv in the Martian atmosphere. Calculations by Krasnopolsky et al. [\(2004\)](#page-11-15) suggested an extended lifetime of several hundred (Earth) years (which suggests that CH4 is uniformly mixed in Mars' atmosphere). A later study by Mumma et al. (2009) , however, proposed a considerably lower CH₄ lifetime of $(0.4–60)$ Earth years. The discrepancy could have arisen due to missing atmospheric CH4 sinks (see, e.g., Lefèvre and Forget [2009;](#page-11-17) Knak Jensen et al. [2014\)](#page-11-18). Whether the CH4 signals on Mars could arise via biology is still debated, Atreya et al. [\(2007\)](#page-9-16) review possible sources. The analysis by Zahnle et al. [\(2011\)](#page-13-3) suggested a smaller abundance ranging from (0 to 3) ppbv on Mars. Spectroscopic measurements by the Curiosity Rover imply 0.7–2.1 ppb CH4 (Webster et al. [2015\)](#page-12-25). This methane may have originated from exogenous delivery (Fries et al. [2016\)](#page-10-24).

Earth-Like Exoplanets and Their Evolution – various studies have suggested planets orbiting M-dwarfs may have up to 1000 times more atmospheric CH4 compared to the modern Earth, for the same surface fluxes (e.g., Segura et al. [2005;](#page-12-7) Rauer et al. [2011;](#page-11-9) Grenfell et al. [2014;](#page-10-21) Rugheimer et al. [2015\)](#page-12-13). Weaker UV emissions from the star lead to less abundant OH, an important sink for CH4, and OH is photolytically produced via the two-reaction sequence: $O_3 + hv(UV) \rightarrow$ O^* + O_2 then: O^* + $H_2O \rightarrow 2OH$. Considering serpentinization as the predominant abiotic source of methane, Guzmán-Marmolejo et al. [\(2013\)](#page-10-25) suggested that N_2 -O₂

dominated atmospheres with CH4>10ppmv could only be produced via biology. Recent laboratory-based studies by McCollon [\(2016\)](#page-11-19) suggested that the abiotic source of CH via serpentinization may have been previously overestimated.

Spectral Detectability – spectral features of CH_4 occur at, e.g., \sim 3.4 and \sim 7.7 μ m (e.g., Rauer et al. [2011;](#page-11-9) Werner et al. [2016\)](#page-13-4). These bands can be mixed with those of H_2O at low spectral resolutions $(R\sim 20)$ for Earth-like atmospheres (Pilcher, [2004\)](#page-11-20). Additional CH₄ bands, e.g., at \sim 1.7 and \sim 2.4 μ m, become evident for abundances of $CH_4 > 100$ ppm (des Marais et al. [2002\)](#page-10-10). Other bands near 1.1μ m, 1.4μ m, and even in the visible region can become apparent at Archean-like abundance levels (e.g., Segura et al. [2003\)](#page-12-6).

Sulfur-Containing Gases

Several sulfur-containing organic molecules (e.g., CH_3SCH_3 , $CH_3S_2CH_3$) have been proposed as atmospheric biosignatures (Domagal-Goldman et al. [2011;](#page-10-26) Vance et al. [2011;](#page-12-26) Pilcher [2004\)](#page-11-20). Their abundance could build up for Earth-like planets in low-UV environments, e.g., orbiting in the HZ of inactive M-dwarf stars. However, these sulfur-bearing gases are challenging to detect due to relatively low abundance and weaker absorption features. Domagal-Goldman et al. [\(2011\)](#page-10-26) showed that methyl groups cleaved from these more complex sulfur-bearing molecules resulted in the production of ethane, which is more spectrally detectable and produces a strong absorption feature near 12 μ m.

Chloromethane

Chloromethane (CH₃Cl) has a mean atmospheric abundance of ~ 0.6 ppb near the Earth's surface with an atmospheric lifetime against chemical removal of up to \sim 2 years (IPCC, [2007\)](#page-10-18). Its global sources and sinks are not well-constrained. The main sources are biological via, e.g., ocean plankton, fungi, and wood rotting, and the sinks include removal via the hydroxyl radical and biological degradation (Harper [2000;](#page-10-27) Keppler et al. [2005\)](#page-10-28). There are also abiotic sources for these gases such as chloride methylation (Keppler et al. 2005). CH₃Cl has been investigated as an atmospheric biosignature in an exoplanet context (e.g., Segura et al. [2005;](#page-12-7) Grenfell et al. [2014\)](#page-10-21). However, the spectral absorption features of $CH₃Cl$ are generally rather weak for the Earth due to low abundance at long wavelengths (e.g., at 13.7 μ m). However, they could become enhanced for planets orbiting inactive Mdwarf stars that allow for longer chemical lifetimes of these gases (see, e.g., Segura et al. [2005;](#page-12-7) Rauer et al. [2011\)](#page-11-9).

Atmospheric Redox Disequilibrium

The focus until now has been on individual atmospheric species proposed as exoplanetary biosignatures. However, the principle of applying redox disequilibrium

as a potential biosignature usually involves the simultaneous presence of two gasphase atmospheric species with differing redox states – one oxidizing (e.g., O_2) and one reducing (e.g., $CH₄$). The underlying principle is that the presence of life is responsible for driving the system away from redox equilibrium.

Cornerstone studies in this area were by Lovelock [\(1965\)](#page-11-21) and Lederberg [\(1965\)](#page-11-22) who suggested that the simultaneous presence of O_2 and CH₄ at Earth-like amounts could be interpreted as a biosignature. These species are associated mainly with cyano- and methanogenic bacteria, respectively. Sagan et al. [\(1994\)](#page-12-27) also proposed that simultaneous observations of CH_4 (a reducer) and O_2 (an oxidizer) in Earth's atmosphere could be interpreted as biosignatures since without life these species would be rapidly removed to much lower abundances. Simoncini et al. [\(2013\)](#page-12-28) accordingly applied a chemical model to quantify such "redox disequilibria" in Earth's atmosphere. False positives for redox disequilibrium include, e.g., ablating micrometeorites (Court and Sephton [2012\)](#page-9-17) and the presence of a moon with its own atmosphere (Rein et al. [2014\)](#page-11-23) because in spatially unresolved observations of exoplanets, spectral signatures of such moons will be difficult to disentangle from their planets. Krissansen-Totton et al. [\(2016\)](#page-11-24) proposed that the simultaneous presence of abundant gas-phase N_2 and O_2 with liquid water as on the modern Earth represents an even stronger chemical disequilibrium than $CH₄$ and $O₂$. Reinhard et al. [\(2017](#page-11-25)**)** discussed some of the challenges of detecting redox equilibrium in the atmospheres of Earth-like exoplanets. One of these challenges can be learned from Earth's history itself: simultaneous O_2 and CH₄ are difficult to detect together because when Earth's O_2 levels have been high, CH₄ levels have been low and vice versa.

Abiotic Earth ("Dead Earth")

When assessing the validity and detectability of atmospheric biosignatures, it is useful to have a benchmark to compare against. One such benchmark is the case of a planet similar to the Earth (in terms of mass, radius, central star, orbit, ocean coverage, etc.) but where life never develops. This is referred to as an "abiotic Earth" or "dead Earth." It is useful to calculate the atmospheric composition, climate, and spectral appearance of such a world to facilitate biosignature candidate screening.

A founding study investigating such worlds was performed by Margulis and Lovelock [\(1974\)](#page-11-26). They investigated two types of dead Earths. First, starting with the modern Earth, the effects of life are removed. In this case, N_2 is oxidized, e.g., by lightning and cosmic rays and is eventually rained out to form the stable aqueous nitrate ion in the ocean. O_2 is removed by deposition and by in situ reaction with reducing gases such as CH4. Second, they considered the evolution of the planet similar to Earth but where life never arose. Margulis and Lovelock [\(1974\)](#page-11-26) calculated a range of $(3-1000)$ mb surface $CO₂$ for their dead Earth scenarios. However, the study by Morrison and Owen [\(2003\)](#page-11-27) suggested that the bulk of the planet's CO_2 inventory (\sim 69 bar) would be returned to the atmosphere. The large range of uncertainty reflects, e.g., poorly constrained knowledge of interactions of life with Earth's carbon cycle. O'Malley-James et al. [\(2014\)](#page-11-28) investigated the future decline of the biosphere as the sun brightens. Their results suggested biomass death at \sim 2.8 Gr in the future on a warmer, wetter planet where photosynthesis stops at $CO₂(g) < 10$ ppmv.

Conclusions and Recommendations

Up to now atmospheric biosignatures in an exoplanet context have mainly focused on understanding the photochemical, climate, and spectral responses of the gasphase species O_2 , O_3 , CH₄, N₂O, and CH₃Cl. Additionally, detection of redox disequilibria is a promising canonical technique which has recently begun receiving more attention in the literature. Furthermore, there is a developing realization regarding the complexity of abiotic sources of potential biosignature gases. This is linked with the notion that each biosignature candidate should be studied in the context of its particular environment – taking into account, e.g., the stellar and particle input, planetary, and orbital parameters.

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