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**Hypothesis Article**

# The Role of $N_2$ as a Geo-Biosignature for the Detection and Characterization of Earth-like Habitats

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## Abstract

Since the Archean, $N_2$ has been a major atmospheric constituent in Earth's atmosphere. Nitrogen is an essential element in the building blocks of life; therefore, the geobiological nitrogen cycle is a fundamental factor in the long-term evolution of both Earth and Earth-like exoplanets. We discuss the development of Earth's $N_2$ atmosphere since the planet's formation and its relation with the geobiological cycle. Then we suggest atmospheric evolution scenarios and their possible interaction with life-forms: first for a stagnant-lid anoxic world, second for a tectonically active anoxic world, and third for an oxidized tectonically active world. Furthermore, we discuss a possible demise of present Earth's biosphere and its effects on the atmosphere. Since life-forms are the most efficient means for recycling deposited nitrogen back into the atmosphere at present, they sustain its surface partial pressure at high levels. Also, the simultaneous presence of significant $N_2$ and $O_2$ is chemically incompatible in an atmosphere over geological timescales. Thus, we argue that an $N_2$-dominated atmosphere in combination with $O_2$ on Earth-like planets within circumstellar habitable zones can be considered as a geo-biosignature. Terrestrial planets with such atmospheres will have an operating tectonic regime connected with an aerobic biosphere, whereas other scenarios in most cases end up with a $CO_2$-dominated atmosphere. We conclude with implications for the search for life on Earth-like exoplanets inside the habitable zones of M to K stars. Key Words: Earth-like exoplanets—Atmospheres—Tectonics—Biosignatures—Nitrogen—Habitability. Astrobiology 19, 927–950.

## 1. Introduction

"ARE WE ALONE in the Universe?" The discovery and characterization of exoplanets around Sun-like stars, which began in 1995 (Mayor and Queloz, 1995), is gradually bringing us closer to answering this fundamental question of humanity. There are, however, two key aspects to consider for finding life as we know it: first we need to detect a large sample of Earth-like planets in their host star's habitable zone, and second we need to detect and confirm biosignatures (*e.g.,* in the form of atmospheric gases).

The evolution of an Earth-like planet and its atmosphere is strongly related to various processes, for example, the planet's formation, its initial volatile and water inventory, the host star's activity controlling the escape of the planetary protoatmosphere, the evolution of the secondary atmosphere, and the planet's impact history (*e.g.,* Halliday, 2003; Lammer *et al.,* 2013a, 2018; Mikhail and Sverjensky, 2014; Wordsworth, 2016; Catling and Kasting, 2017; Zerkle and Mikhail, 2017; Lammer and Blanc, 2018).

As illustrated in Fig. 1, atmospheric percentages of $CO_2$ and $N_2$ on Venus and Mars would be similar to those of present-day Earth, if Earth had not depleted its atmospheric $CO_2$ through weathering during the Hadean (*e.g.,* Walker, 1985; Kasting, 1993; Sleep and Zahnle, 2001). At some point in history, $N_2$ became the dominant constituent in the terrestrial atmosphere. When this happened is a matter of debate, as is the evolution of atmospheric nitrogen. While research on fossilized raindrop imprints suggests that the atmospheric pressure was low in the Archean, probably less than half the present-day value (Som *et al.,* 2012, 2016; Marty *et al.,* 2013; Avice *et al.,* 2018), studies of subduction zones indicate Archean nitrogen partial pressures above the present-day value (Goldblatt *et al.,* 2009; Barry and Hilton, 2016; Johnson and Goldblatt, 2018; Mallik *et al.,* 2018). A better understanding of the evolution of the nitrogen cycle is of crucial importance to address this controversy.

Besides Earth, our solar system features icy moons or dwarf planets lying far beyond the ice line but also possessing $N_2$-dominated atmospheres. For example, Titan (Strobel and

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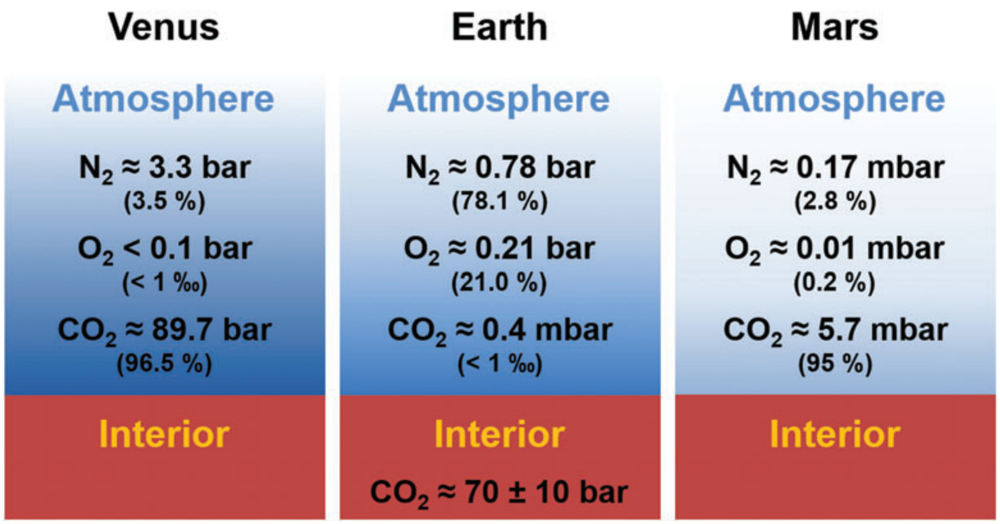


**FIG. 1.** Percentage by volume of total $N_2$, $O_2$, and $CO_2$ contents in the venusian (Oyama *et al.,* 1980), terrestrial (dry air) (NASA, 2017), and martian (Franz *et al.,* 2017) atmospheres. An atmospheric equivalent of about 60–80 bar $CO_2$ is stored in Earth's crust in the form of carbonates (*e.g.,* Ronov and Yaroshevskiy, 1967; Holland, 1978; Walker, 1985; Kasting, 1993). The different blue shades represent the different atmospheric densities.

Shemansky, 1982) has a 1.45 bar atmosphere consisting of 98.4% $N_2$, 1.4% $CH_4$, and 0.1–0.2% $H_2$ (Coustenis and Taylor, 2008). However, the origin of such atmospheres is related to early photolysis of accreted and outgassed $NH_3$ from subsurface $H_2O$-$NH_3$ oceans, leading to a very different environment compared to Earth's $N_2$ atmosphere (Coustenis and Taylor, 2008; Mandt *et al.,* 2009, 2014). In this hypothesis paper, we focus on classical rocky terrestrial planets that originated in an inner planetary system; frozen worlds like Titan, Triton, and Pluto are not considered. Beside these environments, we are aware of alternatively conditioned habitats (*e.g.,* Jones, 2003; Lammer *et al.,* 2009). However, at the moment we have no evidence for non-Earth biochemistries; thus, we focus on Earth-like biospheres.

It is well known that the origin and evolution of life on Earth has a strong influence on Earth's atmospheric composition and climate (Kiehl and Dickinson, 1987; Haqq-Misra *et al.,* 2008; Wolf and Toon, 2013; Kunze *et al.,* 2014; Catling and Kasting, 2017; Charnay *et al.,* 2017). The potentially major role of nitrogen is often overlooked. Recently, Stüeken *et al.* (2016a) simulated atmospheric-biological interactions over geological times on Earth-like planets and even concluded that $N_2$ and $O_2$ in combination could be a possible signature of an oxygen-producing biosphere. This is also supported by thermodynamic studies (Krissansen-Totton *et al.,* 2016a). One should note that nitrogen is an essential element for all life-forms on Earth since it is required, like carbon and phosphorus, for the formation of nucleic acids and proteins.

In order to search for life on extrasolar planets, a set of telltale atmospheric signatures (molecular ''biosignatures'') have been discussed that would allow for the detection and characterization of biospheres (Lovelock, 1975; Segura *et al.,* 2003; Kaltenegger *et al.,* 2007; Grenfell *et al.,* 2007a, 2007b, 2010; Cockell *et al.,* 2009; for a review see Schwieterman *et al.,* 2018). Oxygen is a necessary ingredient for the evolution of complex life-forms on habitable planets, as discussed in detail by Catling *et al.* (2005) and Meadows *et al.* (2018). $O_2$ has long been recognized as a key biosignature, detectable by subsequently produced $O_3$ (Owen, 1980; Léger *et al.,* 1993, 2011; Sagan *et al.,* 1993; Des Marais *et al.,* 2002; Airapetian *et al.,* 2017a). However, several more recent theoretical studies have shown that $O_2$ may also build up abiotically in an exoplanet's atmosphere (Domagal-Goldman *et al.,* 2014; Gao *et al.,* 2015; Harman *et al.,* 2015; Luger and Barnes, 2015; Tian *et al.,* 2014; Wordsworth and Pierrehumbert, 2014). Depending on a planet's gravity and the host star's EUV flux evolution, an important pathway for abiotically raising atmospheric oxygen levels consists of $H_2O$ dissociation followed by hydrogen escape (*e.g.,* Zahnle and Kasting, 1986; Lammer *et al.,* 2011; Luger and Barnes, 2015). If the escape of oxygen is considerably less efficient than that of hydrogen, this could lead to the existence of terrestrial habitable-zone planets with high levels of abiotically accumulated $O_2$, as long as processes that potentially deplete atmospheric oxygen (*e.g.,* surface oxidation) are inefficient. Such a scenario can also happen if the liquid ocean of a terrestrial planet is formed after the EUV saturation phase of the host star (Tu *et al.,* 2015), when the decreased stellar EUV flux is insufficient to remove the dense abiotic oxygen atmosphere. Such $O_2$-rich atmospheres will also produce $O_3$ layers that, accompanied by the detection of $H_2O$ and relatively low $CO_2$ values, could result in potential false positives for life. Grenfell *et al.* (2018) investigated atmospheric $H_2$-$O_2$-combustion as an additional $O_2$ sink and source of water.

Further proposed biosignature molecules include $N_2O$ (Sagan *et al.,* 1993; Segura *et al.,* 2005; Rauer *et al.,* 2011; Rugheimer *et al.,* 2013, 2015; Airapetian *et al.,* 2017a), $CH_4$ (Sagan *et al.,* 1993; Krasnopolsky *et al.,* 2004; Rugheimer *et al.,* 2015; Airapetian *et al.,* 2017a), $CH_3Cl$ (Segura *et al.,* 2005; Rugheimer *et al.,* 2015), $NH_3$ (Seager *et al.,* 2013a, 2013b), sulfur gases and $C_2H_6$ (Pilcher, 2003; Domagal-Goldman *et al.,* 2011), and organic hazes (Arney *et al.,* 2016, 2017). The detection of these species does not necessarily imply that a particular planet is populated by aerobic life-forms as we know them. In order to improve our capacity to interpret these signals in their environmental context, it makes sense to investigate the connection between atmospheric oxygen, Earth's main atmospheric species $N_2$, and the evolution of life.

But which scenarios lead to $N_2$-dominated atmospheres on Earth-like planets, and which do not? Section 2 investigates the role of atmospheric $N_2$ and its coexistence with life as we know it in more detail, while Section 3 discusses partial pressure on Earth in the past. In Section 4, we discuss four atmospheric development scenarios, based on the above-described geobiological interactions, while Section 5 discusses the same for Earth-like planets orbiting M and K stars. Possibilities for the detection of $N_2$-dominated Earth-like atmospheres on exoplanets are discussed in Section 6. In Section 7, we conclude under which conditions $N_2$ accompanied by $O_2$ can be a geo-biosignature, here defined as a biosignature that is strongly linked with tectonic activity.

## 2. Processes Affecting Earth's Early Atmospheric Nitrogen Evolution

### *2.1. Abiotic magmatic surface interactions and steam atmosphere conditions*

In the earliest stages of planet formation, protoplanetary cores can accumulate $H_2$ envelopes (Sekiya *et al.,* 1980a, 1980b; Sasaki and Nakazawa, 1988; Lammer and Blanc, 2018). Due to the captured nebula gas, serpentinization, and accreting chondritic material, crust and atmosphere were strongly reducing and later oxidized during the planet's life (Schaefer and Fegley, 2010). Hydrogen is partly lost during the short very efficient thermal escape phase (''boil-off phase'') and can be completely removed due to EUV-driven hydrodynamic escape (*e.g.,* Gillmann *et al.,* 2009; Lammer *et al.,* 2014, 2018; Johnstone *et al.,* 2015; Fossati *et al.,* 2017; Odert *et al.,* 2018). After the escape of the nebular gas, the deep magma ocean on the planet's surface solidifies and thereby outgasses $H_2O$ and $CO_2$ catastrophically, so that a dense steam atmosphere evolves (Sleep, 2010). Depending on the magma ocean's lifetime as well as the cooling time of this atmosphere, water is either partly lost to space or later condenses to form an ocean (*e.g.,* Elkins-Tanton, 2008, 2012; Hamano *et al.,* 2013; Lebrun *et al.,* 2013; Massol *et al.,* 2016; Salvador *et al.,* 2017).

Due to the catastrophic outgassing during the magma ocean phase, the nitrogen partial pressure could have reached a few hundreds of millibar (Holland, 1984; Turner *et al.,* 1990). Assuming 70 bar of outgassed $CO_2$, plausible for the Earth case, and Earth's C/N ratio of present mid-ocean ridge outgassing obtained by various studies (Zhang and Zindler, 1993; Marty, 1995; Marty and Tolstikhin, 1998; Sano *et al.,* 2001; Coltice *et al.,* 2004; Cartigny *et al.,* 2008; Marty *et al.,* 2013), the total outgassed $N_2$ is in the range of 24–203 mbar (for 500 mbar $N_2$ at least $\sim$170 bar of $CO_2$ would have to be outgassed). One should note that these values are rather a lower estimate, since carbon is known to be well recycled in the present mantle and therefore may distort the C/N ratio for the very early Earth case. Therefore, also 10 times here the estimated values cannot be ruled out. After the outgassing phase, under the still extremely hot surface conditions (>1000 K) in combination with a reducing steam environment, efficient atmospheric $NH_3$ production occurs (Schaefer and Fegley, 2010; Wordsworth, 2016) at a rate that outpaces the dissociation by FUV and EUV radiation (*e.g.,* Holland, 1962; Kuhn and Atreya, 1979; Kasting, 1982, 1993; Zahnle *et al.,* 2013). There are indications by experimental studies that massive direct dissolution into the mantle is then possible in such reduced environments (Solomatov, 2000; Libourel *et al.,* 2003; Kadik *et al.,* 2011). Thus, one can expect that the majority of atmospheric nitrogen is quickly sequestered into the hot surface environment, as illustrated in Fig. 2a (Wordsworth, 2016).

After the magmatic mantle solidified, the steam in the atmosphere eventually condenses to produce a warm liquid $H_2O$ ocean while the atmosphere contains several tens of bar $CO_2$ (*e.g.,* Ronov and Yaroshevskiy, 1967; Holland, 1978;

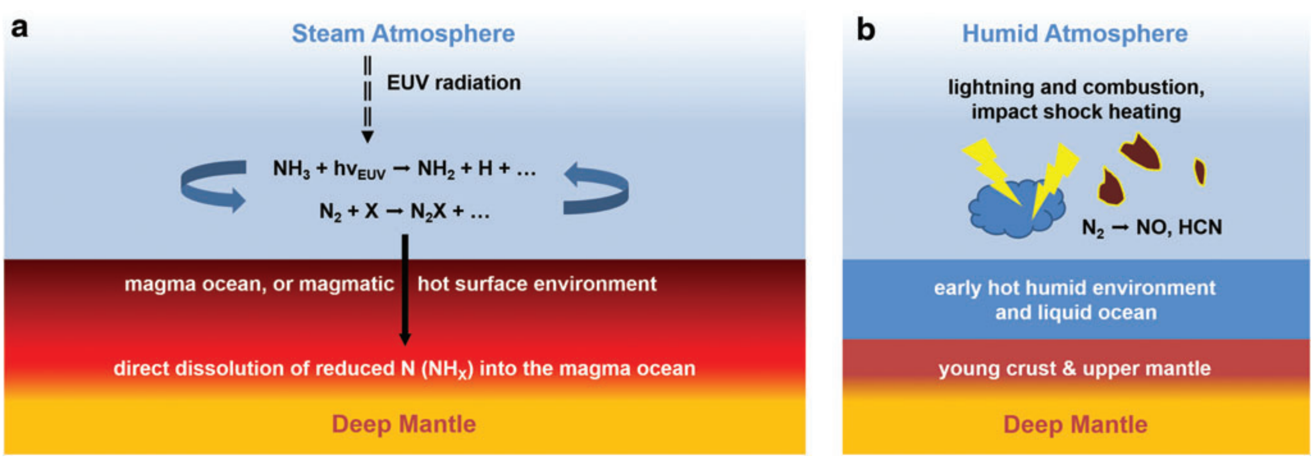


**FIG. 2.** (**a**) Abiotic atmospheric-surface weathering processes capable of transferring atmospheric nitrogen into early Earth's surface and mantle via direct dissolution of reduced nitrogen into the early magma ocean(s). This efficient abiotic mechanism most likely operated on early Venus and Earth during and just after accretion. ''X'' represents a reducing species, such as H (adapted from Wordsworth, 2016). (**b**) Additionally to the magmatic weathering process, atmospheric $N_2$ will also undergo fixation via weathering caused by lightning, shock heating via impactors, and energetic particles in the early steam atmosphere.

Kasting, 1993; Zahnle, 2006; Lammer *et al.,* 2018). Then, as illustrated in Fig. 2b, remaining atmospheric nitrogen is still affected by diverse abiotic fixation processes (see also Section 3; for comparison, Earth's present lightning fixes 10 mbar N in ~10 Myr). However, according to Ranjan *et al.* (2019), an ocean rich in ferrous iron could have re-gassed water solved $NO_x$ back into the atmosphere.

### 2.2. Nitrogen speciation in Earth's upper mantle

Diverse studies of Earth's $N_2$ atmospheric and interior inventories indicate that outgassing of $N_2$ in the first billion years was strongly connected to the planet's thermodynamic evolution (*e.g.,* Busigny and Bebout, 2013; Mikhail and Sverjensky, 2014; Wordsworth, 2016; Zerkle and Mikhail, 2017) and oxidation stages of crust and upper mantle (Kasting, 1993; Delano, 2001; Catling and Claire, 2005; Kelley and Cottrell, 2009; Trail *et al.,* 2011; Catling and Kasting, 2017; Zerkle *et al.,* 2017). Mikhail and Sverjensky (2014) found out that the speciation of $N_2$ in high-pressure, supercritical aqueous fluids in Earth's mantle wedge are the most likely origin of Earth's $N_2$ atmosphere.

Molecular nitrogen is highly incompatible in silicate minerals (Li *et al.,* 2013), while ammonic nitrogen can be moderately compatible in silicates like phlogopite and clinopyroxene (*e.g.,* Watenphul *et al.,* 2010; Li *et al.,* 2013; Mikhail and Sverjensky, 2014; Zerkle and Mikhail, 2017). This is in agreement with experimental data, which indicate that under very oxidizing environmental conditions nitrogen in supercritical fluids remains as dinitrogen ($N_2$) whereas it exists as $NH_3$ under reducing conditions (Canfield *et al.,* 2010). Thermodynamic studies of Mikhail and Sverjensky (2014) indicate that Earth's upper mantle nitrogen inventory is usually present in the form of ammonium ($NH_4^+$) in aqueous fluids and upper mantle minerals. Since Earth developed tectonic activity, subduction of oceanic lithosphere carries oxidized surface rocks and large amounts of water into Earth's upper mantle (Fig. 3; *e.g.,* McCammon, 2005; Hirschmann, 2009; Lammer *et al.,* 2018). This can locally change the redox state to favor $N_2$, which is easily outgassed. Estimates for the start of this process range from 4.35 Gyr ago (Trail *et al.,* 2011) to 3.8 Gyr ago (Delano, 2001).

### 2.3. Development of the geobiological nitrogen cycle

The geobiological nitrogen cycle shows different features before and after oxygen rose in the atmosphere. The major processes affecting nitrogen in both cases are illustrated in Fig. 4. Molecular nitrogen, which was outgassed into Earth's early atmosphere, is chemically inert. Any nitrogen fixation process that could convert nitrogen into more chemically reactive compounds requires high energy.

Abiotic fixation in the early Archean included lightning, high-energy particle interaction, atmospheric shock heating by frequent meteorite impacts, a higher solar UV radiation, and coronal mass ejections related to super flares (*e.g.,* Airapetian *et al.,* 2016). Generally, also throughout later periods until today, nonbiological pathways occur via high-temperature reducing or oxidation reactions of $N_2$ to $NH_x$/HCN/$NO_x$ (Navarro-González *et al.,* 2001; Martin *et al.,* 2007; Parkos *et al.,* 2016), depending on the environment's redox state. These occur during combustion or lightning in the troposphere, followed by conversion into water-soluble molecules (*e.g.,* $HNO_3$) within the atmosphere, which are quickly scavenged by rain.

There is also a biotic fixation pathway since some bacteria are able to reduce atmospheric $N_2$ to $NH_3$ (biological nitrogen fixation, often abbreviated as BNF). Since nitrogen is an ingredient for the building blocks of life, this reduced nitrogen is often assimilated as organic nitrogen ($N_{org}$) by microorganisms and, in more recent times, by plants. Both may also be eaten by other life-forms who either excrete the nitrogen or release it after death. Afterward, this $N_{org}$ is again consumed by bacteria and mineralized into ammonium $NH_4^+$ that can be assimilated again by other organisms (*e.g.,* Boyd and Philippot, 1998; Boyd, 2001; Holloway and Dahlgren, 2002; Mikhail and Sverjensky, 2014; Wordsworth, 2016; Zerkle and Mikhail, 2017).

After oxygen enriched the atmosphere during the Great Oxidation Event (GOE), bacteria have also used $NH_4^+$ as a source of energy on a large scale by oxidizing it to nitrite $NO_2^-$ and to nitrate $NO_3^-$, a process called nitrification (Fig. 4b; Jacob, 1999; Zerkle and Mikhail, 2017; Zerkle *et al.,* 2017). Some bioavailable nitrogen in Earth's ocean is

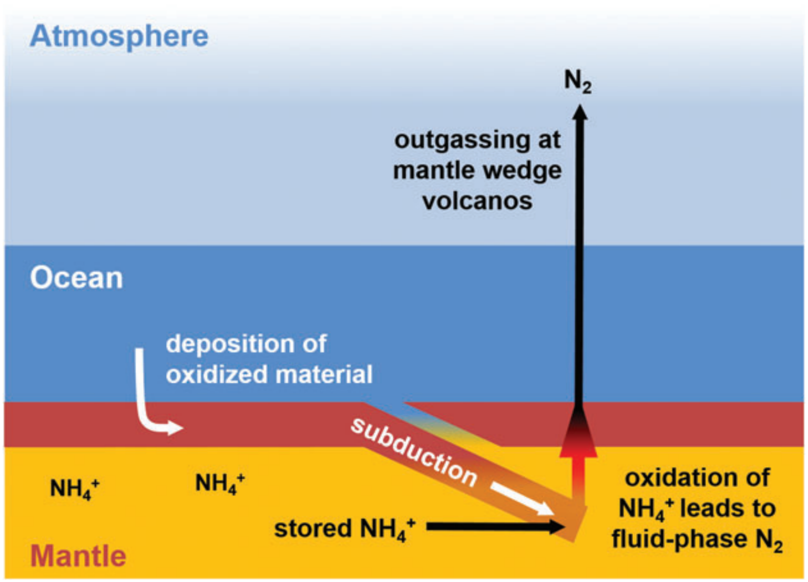


**FIG. 3.** Schematic vertical cross-section through a subduction zone, displaying the geochemical cycle of fluids and outgassing related to mantle wedge areas. Oxidized material is transported via subduction zones into the crust and upper mantle where it reacts with $NH_4^+$ and is hence efficiently outgassed from mantle wedge volcanoes in the form of $N_2$.

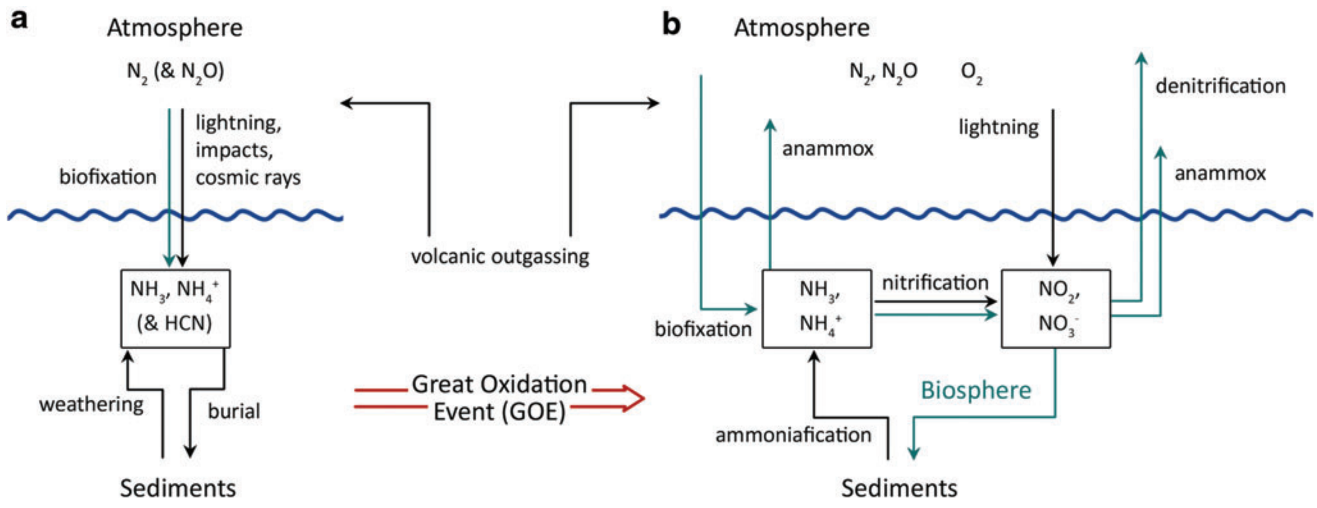


**FIG. 4.** Illustrations of the major nitrogen processes during the Archean and Proterozoic, *i.e.,* before and after the GOE took place, approximately 2.3 Gyr ago. Black and green arrows indicate abiotic and biotic processes, respectively. (**a**) Biogeochemical nitrogen cycle in the Archean before the GOE when anammox and denitrification did not take place. (**b**) As for (a) but after the GOE; a change occurred when oxidation of ammonia to nitrate ($NO_3^-$) and nitrite ($NO_2^-$), so-called ''nitrification,'' set in. These reactions have resulted in the necessary substrate for the reduction of nitrate to atmospheric $N_2$ (denitrification) and anammox to atmospheric $N_2$ via nitrite.

returned to the atmosphere as $N_2$ via denitrification, which means the reduction of nitrate $NO_3^-$ to $N_2$. This microbially facilitated process is performed by heterotrophic bacteria such as *Paracoccus denitrificans*.

Beside these processes, under anaerobic conditions where molecular oxygen is depleted, bacteria can use nitrates as an alternate oxidant to convert organic carbon into $CO_2$ while releasing $N_2$. Another biological process that releases $N_2$ into the atmosphere is called anaerobic ammonium oxidation (anammox), which is the oxidation of $NH_4^+$ with nitrite ($NO_2^-$) that are converted directly into diatomic nitrogen and water. Globally, this process may be responsible for 30–50% of the $N_2$ gas produced in the oceans, which is then released into the atmosphere (Devol, 2003). It is not clear when this process started to play a role in the nitrogen cycle, and it might have been negligible up to the GOE (Som *et al.,* 2016). The requirements for anammox, however, are fulfilled as early as the late Archean (Stüeken *et al.,* 2016b).

### *2.4. Biogenic (and anthropogenic) influences on present Earth's nitrogen cycle*

Although $N_2$ is photochemically inert, nitrogen in the Earth's system was (and still is) efficiently cycled by lifeforms (*e.g.,* phytoplankton, cyanobacteria) at a rate of about $2\times10^{14}$ (g N)/yr (200 [Tg N]/yr) (*e.g.,* Schlesinger, 1997; Jacob, 1999; Galloway, 2003; Cartigny and Marty, 2013), as discussed in Section 2.3 and shown in Fig. 4b. A summary of present total exchange rates of atmospheric nitrogen is provided in Table 1. Tables in the appendix list exchange rates as estimated by various studies.

Today's net nitrogen flux is not undisputed; it is not even clear if there is a net out- or ingassing of nitrogen on Earth (Zerkle and Mikhail, 2017). The massive anthropogenic influence on this system further leads to uncertainties on any conclusion that could be drawn. Human influence destabilizes the well-balanced nitrogen cycle, such that soils

Table 1. Mass Budget and Source Sink Inventory Estimates in the Present Earth's Upper Nitrogen Cycle, Consisting of Atmosphere, Land Biota, Soil and Ocean Biota from the Atmosphere into the Surface/Interior (''-'') and from the Surface into the Atmosphere (''+'')

| *Atmosphere* $3.95\times10^{9}$[a] | *Soil*[b] $1.0\times10^{9}$[a] | *Land biota* $1.0\times10^{4}$[a] | *Ocean* $2.06\times10^{7}$[a] | *Ocean biota* $5.0\times10^{2}$[a] |
|---|---|---|---|---|
| Biofixation | | $-1.2\times10^{2}$ yr$^{-1}$[c] | | $-1.4\times10^{2}$ yr$^{-1}$[c] |
| Rain | $-7.0\times10^{1}$ yr$^{-1}$[c] | | $-3.0\times10^{1}$ yr$^{-1}$[c] | |
| Denitrification | | $+1.1\times10^{2}$ yr$^{-1}$[c] | | $+1.9\times10^{2}$ yr$^{-1}$[c] |
| Biomass burning | | $+5.0$ yr$^{-1}$[c] | | |
| Surface release | $+7.8\times10^{1}$ yr$^{-1}$[c] | | $+1.5\times10^{1}$ yr$^{-1}$[c] | |
| Industry (fertilizers) | $-1.2\times10^{2}$ yr$^{-1}$[c] | | | |

The lower part of the nitrogen cycle including volcanic processes contains rates that are estimated to be at least one order of magnitude smaller than the smallest rates in this table. All values are given in Tg.
[a]Galloway (2003).
[b]The amount of organic nitrogen in soils is estimated to be $2\times10^{5}$.
[c]Fowler *et al.* (2013).
For an overview of different rate estimates, see the tables in the appendix.

and oceans are overloaded with atmospheric nitrogen. This might also be a reason for the rise in $N_2O$ simultaneous to the anthropogenic nitrification over the last decades, which indicates a rise in denitrification. One should note that Earth is a highly dynamic planet with active plate tectonics and varying volcanic activity. The exchange of nitrogen between the atmosphere and the planet's interior is controlled by subduction and volcanism (*e.g.,* Sano *et al.,* 2001; Fischer, 2008). Therefore, the efficiency of nitrogen deposition and outgassing processes that control the atmospheric $N_2$ partial surface pressure is dependent on Earth's inner dynamics and cannot be used linearly for long-time estimates for past or future conditions (making also the studies by Barry and Hilton [2016] and Mallik *et al.* [2018] debatable).

It is important to note that the present-day volcanic outgassing rates of $(1.5 \pm 1.0)$ (Tg N)/yr (Appendix Table A4) cannot balance the atmospheric $N_2$ sinks by fixation of $(430 \pm 60)$ (Tg N)/yr (Table 1, Table A1). Also, if one subtracts the anthropogenic influence, the remaining removal flux is still far too high to be balanced by present volcanic outgassing. Without biological denitrification and anammox that are responsible for a strong return flux, Earth's present-day atmospheric nitrogen of approximately $4 \times 10^9$ Tg would be entirely sequestered within less than 100 Myr (*e.g.,* Cartigny and Marty, 2013; Lammer *et al.,* 2018). Thus, one can conclude that the present-day partial surface pressure of about 0.78 bar is mainly maintained by bacteria, which under anaerobic conditions return $N_2$ from the surface environment to the atmosphere (*e.g.,* Jacob, 1999; Cartigny and Marty, 2013; Wordsworth, 2016; Zerkle *et al.,* 2017).

## 3. The Likely Evolution of the Nitrogen Partial Pressure on Earth

Taking the considerations made in Section 2.1 into account, for Earth one can assume a small percentage of $N_2$ in relation to $CO_2$ to be outgassed from the final magma ocean in the Hadean. In the hot $CO_2/H_2O$ atmosphere, $N_2$ can be efficiently converted into $NH_3$, which subsequently sequesters the majority of nitrogen back into the hot surface environment (Wordsworth, 2016). Abiotic fixation processes such as lightning (*e.g.,* Chameides and Walker, 1981; Navarro-González *et al.,* 2001) that was most likely efficient in a dense humid atmosphere, EUV-related photochemistry (Zahnle, 1986; Tian *et al.,* 2011; Airapetian *et al.,* 2016), frequent meteoritic impacts (Fegley *et al.,* 1986; Chyba and Sagan, 1992; Parkos *et al.,* 2018), and cosmic rays (Navarro-González *et al.,* 1998; Grenfell *et al.,* 2012; Cooray, 2015; Tabataba-Vakili *et al.,* 2016) provided additional energy to fix nitrogen from the atmosphere (see Fig. 2b), even during the postmagmatic surface period. In a scenario where, despite efficient fixation, a relatively high nitrogen partial pressure remains, nitrogen would suffer strong atmospheric escape in cases where it is more abundant than $CO_2$ that cools the thermosphere and hinders escape (see Fig. 9; Tian *et al.,* 2008a; Lichtenegger *et al.,* 2010; Lammer *et al.,* 2011, 2018). The absence of a footprint of such an escape in the atmospheric $^{14}N/^{15}N$ isotope ratio on Earth indicates only percentage levels of $N_2$ compared to $CO_2$ to have been present in the late Hadean (Lichtenegger *et al.,* 2010; Cartigny and Marty, 2013; Avice *et al.,* 2018; Lammer *et al.,* 2018).

All these arguments make nitrogen partial pressures as high as today (or even higher), as assumed in some studies (Goldblatt *et al.,* 2009; Barry and Hilton, 2016; Johnson and Goldblatt, 2018; Mallik *et al.,* 2018), unlikely for this period (Lammer *et al.,* 2008, 2011, 2013a, 2018; Tian *et al.,* 2008a, 2008b; Lichtenegger *et al.,* 2010; Scherf *et al.,* unpublished data). Moreover, higher outgassing fluxes (*e.g.,* Fischer, 2008; our Table A4) that are comparable to subduction fluxes counteract the arguments for a high initial $N_2$ partial pressure presented by Barry and Hilton (2016) and Mallik *et al.* (2018). Thus, a buildup of $N_2$ in the Archean is plausible.

Also during the Archean, one can assume a high number of charge carriers to be present over the wide water ocean surface. Under these conditions, lightning fixation can be efficient (*e.g.,* Rakov and Uman, 2003, 2004; Cooray, 2015). On present Earth, this fixation is estimated to be $(4 \pm 1)$ (Tg N)/yr (Table A1), depleting 100 mbar $N_2$ in 100 Myr. One should be aware that a linear dependency of $NO_x$ production rate to air pressure, as frequently used in models, is not accurate (Navarro-González *et al.,* 2001); therefore, this process might often be underestimated for early Earth. Moreover, if one assumes higher volcanic activity followed by intense discharges in the outgassed $H_2O$-$CO_2$-rich mixture of gases, an additional fixation pathway opens up (Navarro-González *et al.,* 1998). The other above-mentioned fixation processes are still present in the Archean and estimated to fix 1–10 (Tg N)/yr (Navarro-González *et al.,* 1998), whereby EUV-driven photochemistry and the impactor flux decrease in efficiency over time. All these processes can also be responsible for substantial amounts of HCN molecules in a reducing atmosphere, quickly deposited by rain (*e.g.,* Zahnle, 1986; Martin *et al.,* 2007; Parkos *et al.,* 2016). Assuming today's nitrogen outgassing, the buildup of a significant partial surface pressure within this period is not possible—even assuming a factor of 10 higher volcanic activities (Sano *et al.,* 2001; Hilton *et al.,* 2002; see the tables in the appendix). Low-pressure scenarios are also supported by studies of Marty *et al.* (2013) and Som *et al.* (2016), which indicate that the Archean atmosphere had a total surface pressure of 0.23–0.5 bar or even lower.

After the lithospheric oxidation closed up on the GOE level, the nitrogen partial pressure rose dramatically because heterotrophic microorganisms capable of denitrification (or anammox) began to release $N_2$ and therefore to counteract fixation (see Section 2.3). Since this biological recycling involves oxygen, the buildup of a dense $N_2$ atmosphere on early Earth can be correlated with the rise of atmospheric $O_2$ shortly before and during the GOE (*e.g.,* Catling *et al.,* 2005; Lyons *et al.,* 2014; Catling and Kasting, 2017; Lammer *et al.,* 2018).

In summary (see Fig. 5), it can be said that Earth's atmosphere during the late Hadean/early Archean was $CO_2$-dominated but with $CO_2$ decreasing over time (Hessler *et al.,* 2004; Kanzaki and Murakami, 2015). As soon as the reduced nitrogen in the upper mantle could be oxidized through subduction (Catling *et al.,* 2001; Kump *et al.,* 2001; Lyons *et al.,* 2014; Aulbach and Stagno, 2016), $N_2$ was outgassed via volcanoes at C/N ratios comparable to that of today. After the rise of life, greenhouse gases such as $CH_4$, $N_2O$ (*e.g.,* Catling *et al.,* 2001; Airapetian *et al.,* 2016; Catling and Kasting, 2017; Lammer *et al.,* 2018), and a still substantial

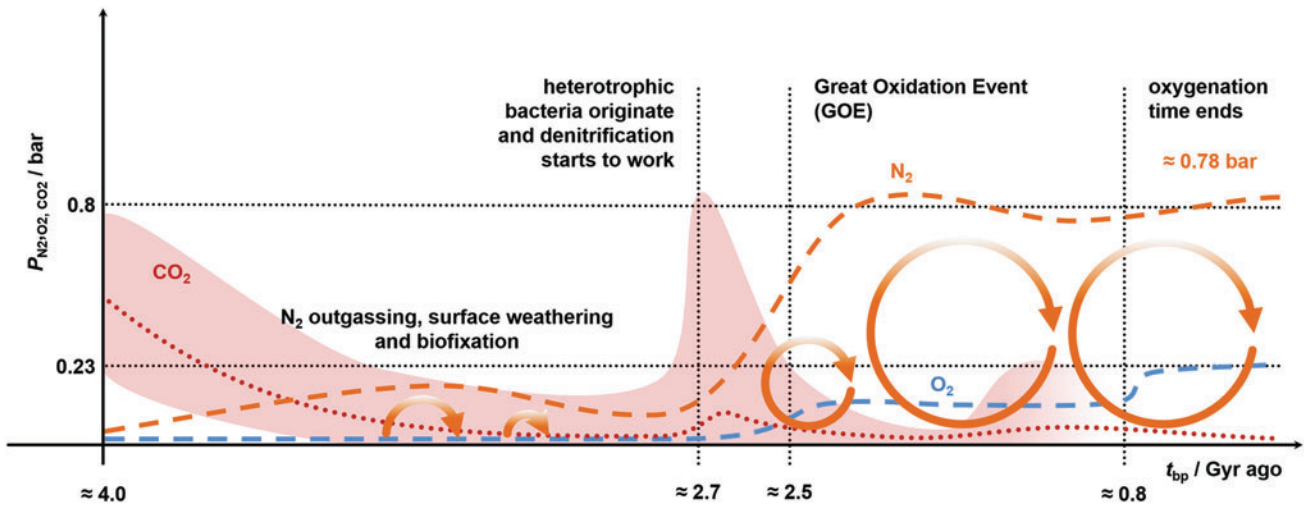


**FIG. 5.** Illustration of the $CO_2$, $N_2$, $O_2$ surface partial pressure evolution on early Earth since about 4 Gyr ago. The ranges for $CO_2$ in light red follow roughly the measurements for 2.77–1.85 Gyr by Kanzaki and Murakami (2015). Before about 4 Gyr ago, nitrogen was mainly sedimented in the oceans and stored as $NH_4^+$. After the crust and upper mantle environment became oxidized, nitrogen in the form of $N_2$ was efficiently released into Earth's atmosphere via mantle wedge volcanism above subduction zones (*e.g.,* Mikhail and Sverjensky, 2014; Zerkle and Mikhail, 2017). In the later Archean, biological fixation may have lowered the partial pressure. $N_2$ then rose to the present values, when heterotrophic microorganisms responsible for denitrification led to the modern geobiological nitrogen cycle. This pressure jump was related to the GOE when oxygen was effectively released into the atmosphere (*e.g.,* Catling *et al.,* 2005; Lyons *et al.,* 2014; Catling and Kasting, 2017; Lammer *et al.,* 2018). The semicircles and the full circles illustrate the nitrogen cycle in the early form (drawn in Fig. 4a) and in the completed form (Fig. 4b), respectively.



amount of $CO_2$ (Kanzaki and Murakami, 2015) kept the surface environment above freezing, which is also indicated by recent 3D global circulation models (Feulner, 2012; Wolf and Toon, 2013; Charnay *et al.,* 2017). Thus, high atmospheric pressures in order to warm the surface by pressure broadening (*e.g.,* Goldblatt *et al.,* 2009; Johnson and Goldblatt, 2018) are not necessary. Finally, at the GOE, $O_2$ built up catastrophically in the atmosphere, and the $N_2$ geobiological cycle changed to its modern form (*e.g.,* Zerkle and Mikhail, 2017; Zerkle *et al.,* 2017), so that the surface pressure rose to the present level. The high nitrogen partial pressure on Earth is then directly linked to its biosphere but necessarily combined with oxygen as another bulk gas.

## 4. Hypothetical Scenarios for the Evolution of $N_2$ Atmospheres

The following scenarios consider hypothetical terrestrial planets that have accreted a mass and size similar to those of Earth, so that one can expect that the protoplanetary core did not accumulate a huge amount of nebular gas that would not be lost during the planet's lifetime (*e.g.,* Lammer *et al.,* 2014, 2018; Johnstone *et al.,* 2015; Owen and Mohanty, 2016; Fossati *et al.,* 2017; Lehmer and Catling, 2017; Lammer and Blanc, 2018). We further assume that the planets orbit around a Sun-like star inside the habitable zone.

After the majority of a surrounding $H_2$-envelope is lost, one can expect that volatiles ($H_2O$, $CO_2$, CO, $NH_3$, HCN, etc.), which have been delivered in the early phase of the accretion via chondrites from the outer planetary system, can be outgassed from a magma ocean formed at the protoplanetary surface. When the final magma ocean solidifies, a dense steam atmosphere builds up until the water vapor condenses after 1–2 Myr and liquid oceans form (Elkins-Tanton, 2012; Hamano *et al.,* 2013; Lebrun *et al.,* 2013; Massol *et al.,* 2016; Salvador *et al.,* 2017).

A large fraction of the accreted water on a planet inside the habitable zone will eventually exist in liquid form on the planet's surface and in its interior, which then features a hydrous mantle transition zone (Pearson *et al.,* 2014; Schmandt *et al.,* 2014; Plümper *et al.,* 2017). In addition to a suitable amount of short-lived radioactive isotopes, water influences the thermal evolution and rock mechanics in the planet's mantle during the later evolutionary stages, including the possibility as to whether plate tectonics will start to operate or not (*e.g.,* Hopkins *et al.,* 2008, 2010; Shirey *et al.,* 2008; Korenaga, 2013).

Based on the above evolution scenarios, we consider the following cases and their impact on the evolution of $N_2$ atmospheres:

4.1. Stagnant-lid regime world: Neither plate tectonics nor life evolve, although the planet has a liquid water ocean on its surface.

4.2. Anoxic tectonic world: Plate tectonics evolve, and a liquid water ocean is situated on the planet's surface, but no life or only anoxic life-forms originate.

4.3. Oxic tectonic (Earth-analog) world: Origin and evolution scenario as expected to have occurred on Earth up to the present day.

4.4. Entirely extinct world: All conditions similar to present Earth, but all life-forms suddenly become extinct.

### *4.1. Stagnant-lid regime world*

In the first scenario, we investigate how Earth's atmosphere may have evolved if the initial conditions in the early mantle did not favor plate tectonics. Plate tectonics is considered crucial for maintaining the activity of the carbon-silicate cycle over geological timescales hence stabilizing Earth's climate. As discussed above (Section 2.2), the absence of subduction on a terrestrial planet has a profound influence on the chemistry in the lithosphere, which affects outgassing and hence the atmosphere. Figure 6 illustrates the evolution of such a planet's atmosphere.

After the evaporation of a possible thin nebular-based $H_2$ envelope, a steam atmosphere formed by catastrophic outgassing during magma ocean solidification would have contained mainly $H_2O$, $CO_2$, and, to a lesser extent, nitrogen (*e.g.,* Elkins-Tanton, 2008, 2012). One can expect that atmospheric nitrogen was efficiently weathered in this environment via fixation by lightning, meteoritic impactors, and cosmic rays, as described in Section 2.1.

Contrary to a Venus-like case at 0.7 AU, where $H_2O$ likely remained in vapor form, at 1 AU water vapor likely condensed to form a liquid ocean within ~2 Myr (Hamano *et al.,* 2013; Lebrun *et al.,* 2013; Massol *et al.,* 2016; Salvador *et al.,* 2017). Depending on pH level, surface temperature, pressure, and alkalinity, such oceans can dissolve atmospheric $CO_2$ leading to possible seafloor weathering (Walker *et al.,* 1981; Pierrehumbert, 2010; Kitzmann *et al.,* 2015; Krissansen-Totton and Catling, 2017; Coogan and Gillis, 2018; Krissansen-Totton *et al.,* 2018a). In the case of a 1 bar $CO_2$ atmosphere, some 30–300 mbar of $CO_2$ remains in the atmosphere (Walker, 1985; Jacob, 1999). Furthermore, $CO_2$ can additionally be weathered via processes such as sequestration of carbon dioxides by carbonate minerals (*e.g.,* Alt and Teagle, 1999; van Berk *et al.,* 2012; Tosi *et al.,* 2017). As illustrated in Fig. 6, atmospheric $CO_2$ therefore decreases during the first few hundred million years.

Since $CO_2$ is a greenhouse gas and thermospheric IR-cooler, it hinders strong thermal atmospheric escape of nitrogen during the EUV active phase of the young Sun/star. If the $CO_2$ pressure drops to values below those of $N_2$, escape to space can emerge as described in Section 3.

Tosi *et al.* (2017) modeled the outgassing of $CO_2$ and $H_2O$ of a ''stagnant-lid Earth'' but did not include a magma ocean or the catastrophically outgassed steam atmosphere (Elkins-Tanton, 2008, 2012; Hamano *et al.,* 2013; Lebrun *et al.,* 2013; Massol *et al.,* 2016). In their model scenarios, secondary outgassed $CO_2$ builds up to surface pressures of ~1.5 bar or less (through weathering) for reducing conditions in the upper mantle (Tosi *et al.,* 2017). For oxidizing conditions, they obtained Venus-like $CO_2$ atmospheres with surface pressures between 100 and 200 bar.

Depending on the efficiency of abiotic $CO_2$ atmosphere-ocean/surface weathering processes, it is possible that the oxidation state on stagnant-lid Earths remains very low due to the missing subduction and related recycling of water and transport of oxidized material into the lower crust and upper mantle (*e.g.,* McCammon, 2005; Tosi *et al.,* 2017). In the case of a Venus-like or stagnant-lid Earth-like planet at closer orbital separations, $H_2O$ may never condense, that is, no liquid oceans on the planet's surface. If the young host star's EUV flux is not too high, some residual $O_2$ may remain in the atmosphere as a product of $H_2O$ dissociation, while the hydrogen atoms escape hydrodynamically (Zahnle and Kasting, 1986). The remaining oxygen and atmospheric nitrogen could have been incorporated into the planet's hot magmatic crust, where they oxidized the upper mantle (Gillmann *et al.,* 2009; Hamano *et al.,* 2013; Kurosawa, 2015; Lichtenegger *et al.,* 2016; Wordsworth, 2016; Lammer *et al.,* 2018). Under such conditions, the highly oxidized surface material can be mixed with reduced, nitrogen-rich material. This implies a change in carbon from a reduced form

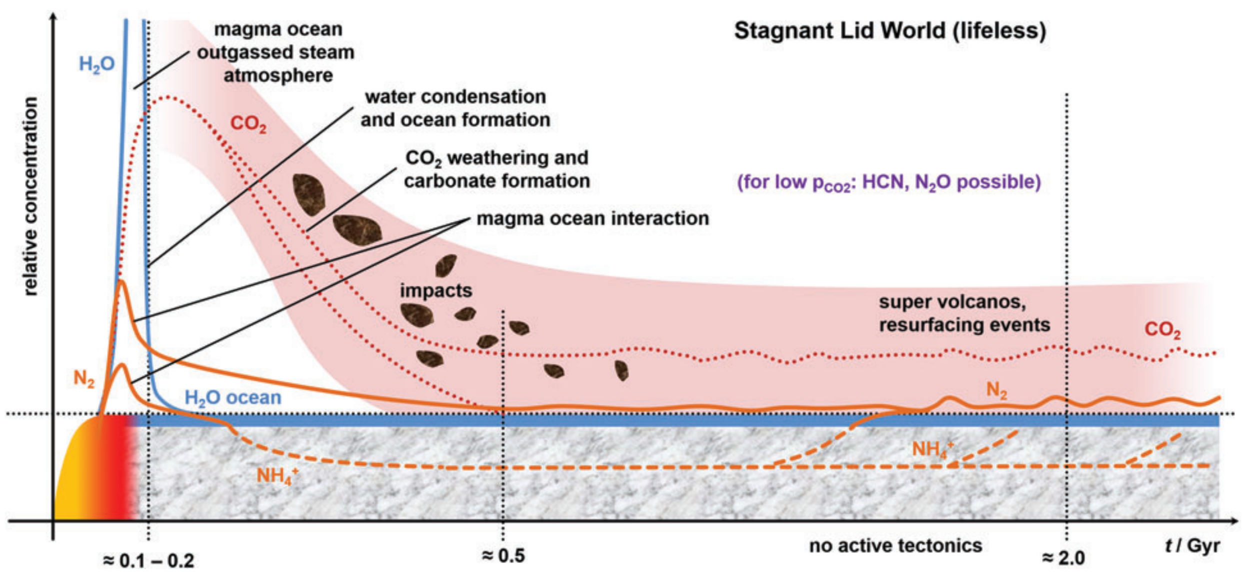


**FIG. 6.** Illustration of the atmospheric evolution of $N_2$ (orange), $CO_2$ (red), and $H_2O$ (blue) for a stagnant-lid regime world. To show the diversity of the pathways for both $N_2$ and $CO_2$ scenarios, lines are respectively drawn; for $CO_2$ a range is provided (red shaded area). After surface temperatures had dropped, $H_2O$ condensed and formed a liquid ocean. $N_2$ and $CO_2$ are weathered out, while a fraction of the $CO_2$ remains in the atmosphere. Oxidation of the crust and upper mantle is inefficient in such a scenario, and oxidized material does not easily get in contact with the $NH_4^+$ in the planet's interior. No efficient outgassing of $CO_2$ and $N_2$ occurs, and the planet most likely evolves a thin martian-like atmosphere whose concentration and related surface pressure may fluctuate depending on the efficiency of $N_2$ and $CO_2$ atmosphere-surface weathering, volcanic activity, availability of additional greenhouse gases (*e.g.,* $N_2O$, $H_2O$, $CH_4$), and possible resurfacing events.

into a more volatile form, which is more easily outgassed. The oxidation at the surface depleting residual oxygen from hydrodynamic escape can potentially explain the 3.4 times greater atmospheric $N_2$ inventory on Venus compared to Earth (Wordsworth, 2016).

In the absence of this residual oxygen from the escaping $H_2O$-related hydrogen, as illustrated in Fig. 6, no fast and efficient oxidation stage evolves. Due to this—as well as the above-mentioned absence of subduction zones and efficient reintroduction of oxidized material into the upper mantle—the secondary outgassed $CO_2$ abundance most likely remains much smaller (*i.e.,* $\leq 1$ bar) on an Earth-like compared to a Venus-like planet (Tosi *et al.,* 2017). Their results further suggest that at 1 AU surface temperatures generally allow the presence of liquid water over almost the entire planetary lifetime. The outer and inner edge of the habitable zone in such stagnant-lid regime worlds is mainly influenced by the amount of outgassed $CO_2$ and other possible greenhouse gases. As mentioned above, these initially $CO_2$-dominated atmospheres can partly dissolve into an ocean.

In conclusion, without massive cycling and a return flux by biological activity, atmospheric nitrogen would be removed to the surface and converted to $NH_4^+$ within a few tens of millions of years (Galloway, 2003; Cartigny and Marty, 2013; Lammer *et al.,* 2018). Since any active tectonics is assumed to be absent in this scenario, oxidized material does not easily come into contact with the $NH_4^+$ in the planet's interior. Therefore, similar to $CO_2$, no efficient outgassing of $N_2$ occurs so that the planetary atmosphere evolves to be thin with partial pressures in the range of a few millibar to tens of millibar, dominated by $CO_2$ and $N_2$.

### 4.2. Anoxic tectonic world

In the second scenario, we assume an Earth-like planet that has developed active tectonics, but either no life or only anoxic life-forms originated. Figure 7 illustrates the planet's atmospheric evolution under such an assumption. Similar to the stagnant-lid case, a steam atmosphere related to the magma ocean solidification process catastrophically outgasses (mainly) $H_2O$, $CO_2$, and (to a lesser extent) $N_2$. Then, water vapor condenses after <2 Myr (at 1 AU) followed by atmosphere-surface interaction processes that weather most of the $CO_2$ and the $N_2$ from the humid atmosphere.

Due to active tectonics, the planet's lithosphere will be gradually oxidized in this scenario, because the oxidized surface material can efficiently enter the crust and upper mantle. Nitrogen can then significantly be released via arc-volcanoes in the form of $N_2$ (*e.g.,* Mikhail and Sverjensky, 2014). This can counteract abiotic fixation such as by lightning and impacts (described in Section 2.3) and lead to the buildup of nitrogen as a bulk gas, even with pressures higher than those of $CO_2$. According to Chameides and Walker (1981), a key parameter that determines the fixation for atmospheric nitrogen is then the ratio of C to O atoms in the atmosphere. Atmospheres with the C/O abundance ratios >1 have large HCN fixation rates compared to NO yields and vice versa.

Anoxic life-forms capable of fixing nitrogen can result in its significant atmospheric depletion. According to estimates given in Jacob (1999), this depletion has timescales up to 15 Myr. If only anoxic life originates, then nitrogen fixation by life-forms, lightning, and cosmic rays will be dominant, and, because of the absence of denitrification, a nitrogen partial

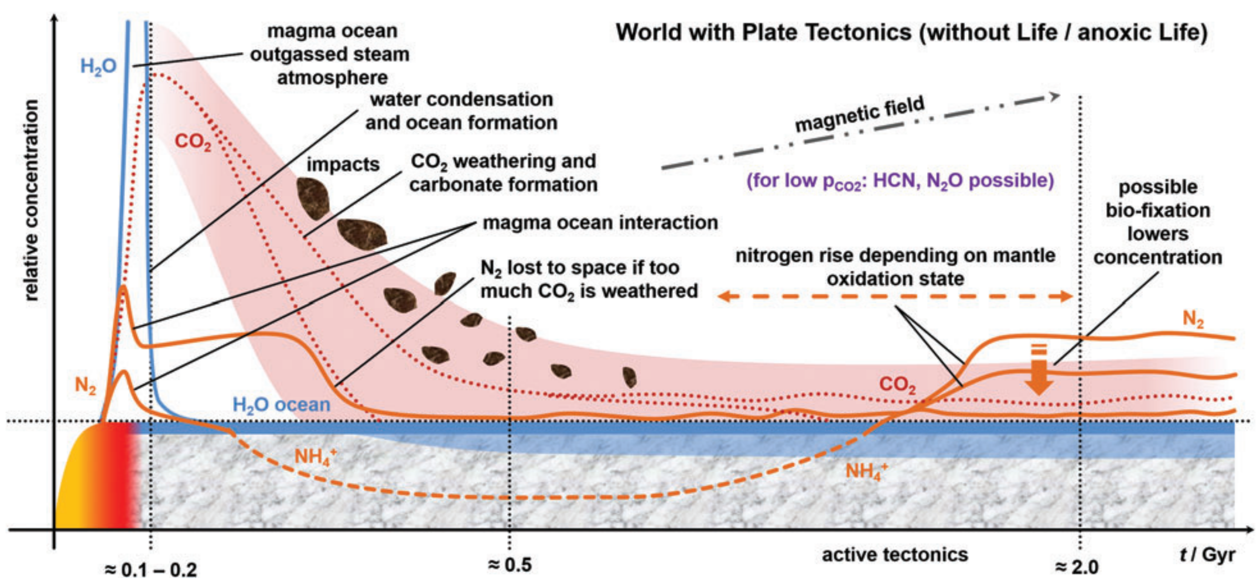


**FIG. 7.** Illustration of the atmospheric evolution of $N_2$ (orange), $CO_2$ (red), and $H_2O$ (blue) for a world where no life (or anoxic life) originated. To show the diversity of the pathways for both $N_2$ and $CO_2$ scenarios, lines are respectively drawn; for $CO_2$ a range is provided (red shaded area). $H_2O$ condensed and formed a liquid ocean, $CO_2$ and $N_2$ are weathered out of the atmosphere, plate tectonics operates and transports oxidized material into the lithosphere of the planet so that nitrogen can be efficiently outgassed later via subduction zone volcanoes in the form of $N_2$. The nitrogen partial pressure in the long term depends on the abiotic fixation efficiency. With anoxic life, denitrification does not operate under these assumptions, and the buildup of a dense $N_2$-dominated atmosphere is unlikely.

pressure similar to that of today is not likely to build up over geological time spans.

Stüeken *et al.* (2016a) simulated similar cases, but with the assumption of (a) today's $N_2$ partial pressure at the very beginning of the planet's origin and (b) its total recovery after being depleted. Both assumptions may not be realistic scenarios: (a) discussed in Section 2.2 and Fig. 2, and (b) discussed in Section 2.4 and Table 1. Also, a model by Laneuville *et al.* (2018) resulted in high atmospheric nitrogen partial pressures (0.5–8 PAL) for a completely lifeless world. One should note that they assumed an active carbon-silicate cycle like on modern Earth and rather low abiotic fixation rates (see lightning rate discussion in Section 3). Nevertheless, their study suggests possible pathways for an abiotic $N_2$ atmosphere with plate tectonics but without $O_2$. In case of anoxic life, as illustrated in Fig. 7, biogenic fixation lowers the nitrogen partial pressure.

According to Kasting *et al.* (1993), nitrogen reducing at mid-ocean ridges could release $N_2$ back into the atmosphere. For such a process, one needs necessarily modern-style plate tectonics. However, this should be modeled in detail to investigate, if it is efficient enough to keep $N_2$ as a major atmospheric constituent. Nevertheless, the $O_2$ surface partial pressure would not rise in such a scenario.

Finally, under the conditions assumed here, an atmosphere will most likely evolve to a thin $CO_2$-dominated atmosphere similar to the stagnant-lid scenario, but with likely less fluctuations in the atmospheric abundance, since no resurfacing events or other catastrophic processes may occur.

### *4.3. Oxic tectonic (Earth-analog) world*

Here, we describe a world with both plate tectonics and life-forms, that is, a planet like Earth. We proceed on the assumption that life arose some 3.7–4.0 Gyr ago (<0.9 Gyr after the planet's formation) and has contributed to the development of the surface and the atmosphere ever since.

On Earth, we know that plate tectonics is a fundamental process, required not only to gradually oxidize the lithosphere (Section 2.2) but also influencing diverse outgassing rates while recycling sediments and further fractionating the crust (*e.g.,* Elkins-Tanton, 2005; Hacker *et al.,* 2011). Beginning with plume-driven circulation, this phenomenon may be closely tied to life, since it provides fundamental chemical preconditions for the atmosphere such as the composition and therefore the oxidation state (*e.g.,* Höning *et al.,* 2014; Höning and Spohn, 2016; Lee *et al.,* 2016).

In the very beginning, such a planet develops similarly to the anoxic world scenario, but after the origin of life, the influence of biotic processes begins to set in.

In the post-steam atmospheric period, a fraction of the $CO_2$ can remain in the atmosphere as a greenhouse gas and thermospheric IR-cooler, inhibiting escape to space and keeping the surface temperature above freezing. Later, the higher solar luminosity and additional greenhouse gases (*i.e.,* $N_2O$, $H_2O$, $CH_4$) partially take over this task. In this period, outgassed (or residual) $N_2$ is not only fixed abiotically, it is also reduced by biotic fixation (*e.g.,* Kharecha *et al.,* 2005; Haqq-Misra *et al.,* 2008; Zerkle and Mikhail,

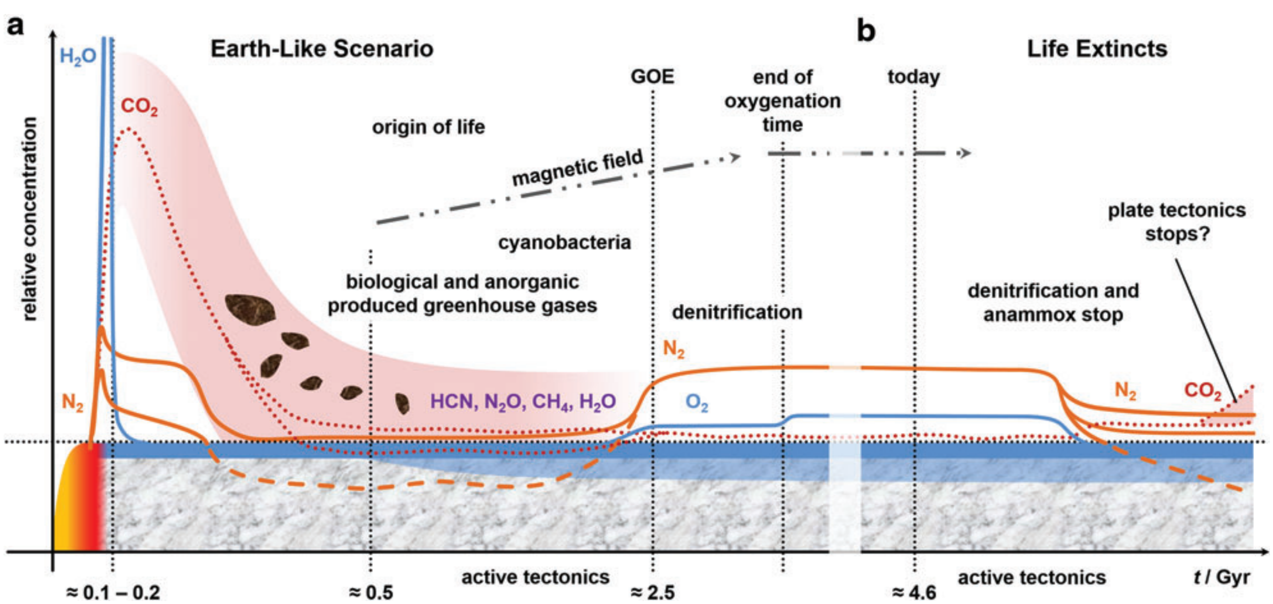


**FIG. 8.** Illustration of the atmospheric evolution of $N_2$ (orange), $CO_2$ (red), $O_2$ (light blue), and $H_2O$ (deep blue) for an Earth-analog world from its origins to a possible future. To show the diversity of the pathways for both $N_2$ and $CO_2$ scenarios, lines are respectively drawn; for $CO_2$ a range is provided (red shaded area). (**a**) Due to plate tectonics and liquid water, atmospheric $CO_2$ will be weathered from the atmosphere and transformed into carbonates. A fraction of the $CO_2$ remains in the atmosphere. As soon as the planet's crust and upper mantle oxidize, $N_2$ is released efficiently via volcanoes. After the origin of life, the oxidation state is enhanced with a strong buildup of $O_2$ during the GOE. Since then, $O_2$ has become a major constituent of the atmosphere, and life-forms began to balance the $N_2$ surface partial pressure to the present level. (**b**) When life becomes extinct and denitrification stops, the atmospheric nitrogen is weathered into the surface within a few tens of millions of years, so that the atmosphere will evolve into a thin $CO_2$- or/and $N_2$-dominated atmosphere, similar to that of Section 4.2. In the case that plate tectonics stops, $CO_2$ rises again, leading to a final composition comparable to that of Section 4.1.

2017), as described in Section 2.3. However, the relatively low nitrogen partial pressure in combination with the difficulty of reintroducing already sedimented nitrogen into the anoxic nitrogen cycle constrained the further development of life. Thus, an equilibrium between available (therefore outgassed) nitrogen and the number of life-forms, which can process and therefore fix it, is established, particularly if one considers a possible uptake of abiotically fixed nitrogen within the oxygen-deficient oceans. The fixed nitrogen is stored in the biosphere and in sediments, as long as no recycling occurs. The above ideas are graphically portrayed in Fig. 8a.

Between 2.7 and 2.2 Gyr ago ($\sim$2 Gyr after the planet's formation), not only plate tectonics changes fundamentally to become the process that is observed on Earth today, but also the atmosphere changes dramatically and the chemical cycles rearrange (*e.g.,* Condie and O'Neill, 2010; Catling, 2014; Zerkle *et al.,* 2017). This transition, known as the GOE, provides oxygen as a nutrient in biological processes and leads to nitrogen-releasing processes such as denitrification (see Fig. 2 and Section 2.2 and references therein). However, for bacteria that are suited to a reducing environment, this implies an existential crisis requiring adaption for survival (*e.g.,* Schopf, 2014; Schirrmeister *et al.,* 2015). Via weathering and uptake processes, sedimented nitrogen can also be cycled back into the ocean and atmosphere, boosting the accumulation of atmospheric $N_2$ (and $N_2O$). At the end of the oxygenation time (see Catling *et al.,* 2005), further oxygen sinks are filled up, followed by a second but smaller rise in $O_2$ partial pressures. A new equilibrium between available and fixed nitrogen is established. At later stages, the $N_2$ abundance could be quite constant as was the case for the last 600 Myr on Earth (Berner, 2006). Finally, the atmosphere is predominantly composed of nitrogen and oxygen, where the latter is significantly less abundant though still being an important constituent (0.78 and 0.21 bar on Earth).

### 4.4. Entirely extinct world

In the fourth scenario, we investigate an Earth-like evolution but assume that all life-forms become extinct in the (far) future (illustrated in Fig. 8). In this case, the earlier atmospheric evolution during the first few hundred million years follows the mechanisms with active plate tectonics as discussed in the previous chapter. Cyanobacteria, phytoplankton, and so on have evolved, permitting a massive recycling of the secondary outgassed atmospheric $N_2$ by biological activity due to denitrification and anammox (*e.g.,* Galloway, 2003; Cartigny and Marty, 2013; see also the previous section).

As long as the planet is populated by life-forms that efficiently cycle $N_2$ back into the atmosphere, it will be $N_2$-dominated. However, when life becomes extinct, denitrification and anammox stop. The atmosphere no longer experiences strong return fluxes of nitrogen, and $N_2$ and $O_2$ become fixed as $NO_x$ primarily by lightning. Then nitrogen is almost completely sequestered into the surface and dissolved into the ocean within about 100 Myr (*e.g.,* Lovelock and Margulis, 1974; Jacob, 1999; Galloway, 2003; Cartigny and Marty, 2013; Lammer *et al.,* 2018). After the life-related oxygen disappears, $N_2$ continues to be fixed further, in which the required oxygen is supplied by $H_2O$ or $CO_2$. Similar to the two other cases discussed before, the atmosphere will then, ignoring possible argon, evolve into a $CO_2$-dominated atmosphere (Lovelock and Margulis, 1974; Margulis and Lovelock, 1974).

A significant release of nitrogen at mid-ocean ridges (Kasting *et al.,* 1993), also discussed in Section 4.2, is even more uncertain considering the linkage between a biosphere and plate tectonics (Höning *et al.,* 2014; Höning and Spohn, 2016). Keeping this in mind, an alteration in modern-style plate tectonics is feasible after life ceases to exist. Further, if plate tectonics stops, a condition similar to the stagnant-lid regime world could evolve. Generally, this implies that only the simultaneous dominant presence of $N_2$ and $O_2$ in the atmosphere represents a geo-biosignature (see also Stüeken *et al.,* 2016a).

## 5. Earth-like Planets in Habitable Zones of M- and K-Type Stars

The atmospheric evolution scenarios discussed above were for planets orbiting solar-like G-type stars. Here, we briefly discuss similar scenarios for Earth-like planets with or without active plate tectonics, which evolve inside habitable zones around active young M and K stars. Atmospheres of such planets, situated in their respective habitable zone around a M- or K-type star, would be subject to extreme X-ray and EUV fluxes for a much longer time than if they were orbiting a G-type star (*e.g.,* Gershberg *et al.,* 1999; Scalo *et al.,* 2007; Loyd *et al.,* 2016; Youngblood *et al.,* 2016). Furthermore, dense stellar plasma fluxes ejected by coronal mass ejections (Khodachenko *et al.,* 2007; Lammer *et al.,* 2007, 2009) can initiate various atmospheric escape processes. This affects the planet's habitability in terms of surface water inventory, atmospheric pressure, greenhouse warming efficiency, and the dosage of the UV surface irradiation (*e.g.,* Lammer *et al.,* 2007; Scalo *et al.,* 2007; Luger *et al.,* 2015; Airapetian *et al.,* 2017b).

Besides the exposure of high EUV fluxes and dense stellar plasma, one can expect that Earth-like planets inside the habitable zone of these stars are either partially or totally tidally locked, resulting in smaller magnetospheres relative to that of Earth's (Fig. 9; Khodachenko *et al.,* 2007). A recent model by Kislyakova *et al.* (2017, 2018) suggested that some M star habitable zone planets could be strongly affected by electromagnetic induction heating during their early evolution, caused by the star's rotation and the planet's orbital motion. In such a case, induction heating can melt the planetary mantle, hence inducing extreme volcanic activity and constant resurfacing events, similar to Jupiter's moon Io, though this effect would be somewhat smaller for habitable-zone planets.

Moreover, the atmospheres and oceans of tidally locked planets may freeze out to form a permanent ice cap on the dark side of the planet. According to Joshi (2003), $CO_2$-dominated atmospheres with pressures of about 100 mbar may be sustained on tidally locked Earth-like planets through circulation between the day and night sides. In addition, that study suggested that thicker $CO_2$ atmospheres of about 1–2 bar would allow for liquid water on the planet's surface, which was also confirmed by Shields *et al.* (2013), who assumed such planets in the outer edge of M star habitable zones. Further, cloud feedback could expand the habitable zone of tidally locked planets significantly (Yang *et al.,* 2013). The formation of a biosphere requires the presence of

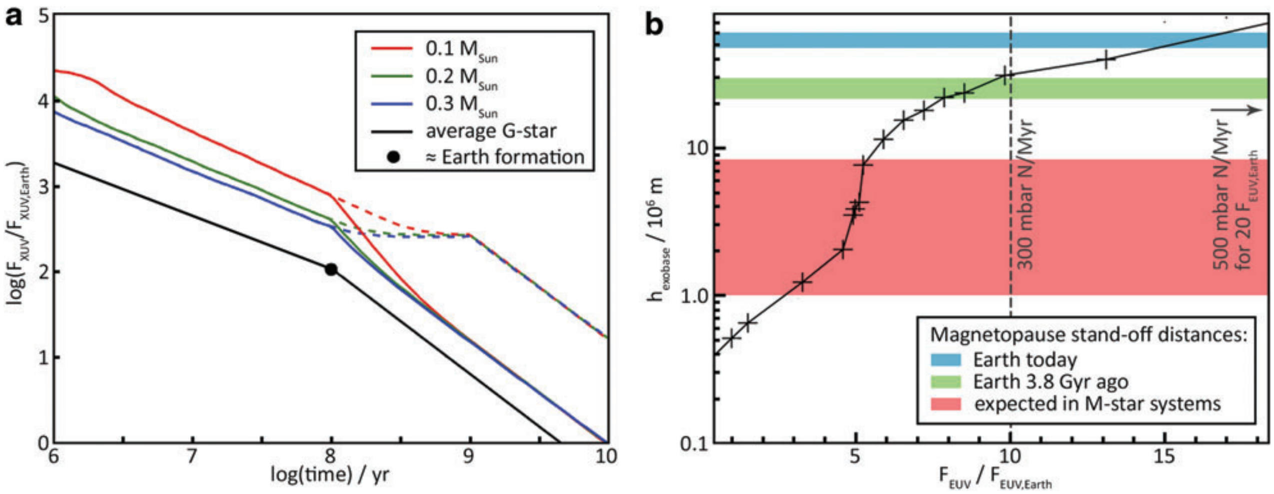


**FIG. 9.** (**a**) Incident XUV flux over time for planets in the habitable zone of M-type stars and of a moderate rotating G-type star, normalized to Earth's present flux. Scenarios for an EUV saturation time of 0.1 Gyr are drawn solid, whereas dashed lines correspond to 1.0 Gyr. Figure adapted from Luger *et al.* (2015). (**b**) Variation of the exobase altitude relative to the Earth-normalized incident EUV flux after Tian *et al.* (2008a) in relation to planetary magnetopause stand-off distances under different stellar wind conditions (data for M-type stars: Khodachenko *et al.,* 2007; data for Earth: Lichtenegger *et al.,* 2010). A nitrogen escape rate of 300 mbar/Myr is expected for 10 $F_{\mathrm{EUV,Earth}}$ and 500 mbar/Myr for 20 $F_{\mathrm{EUV,Earth}}$ (Lichtenegger *et al.,* 2010), respectively.



a stable atmosphere and water inventory. However, various previous studies (Khodachenko *et al.,* 2007; Lammer *et al.,* 2007, 2013b; Airapetian *et al.,* 2017b) indicate that Earth-like planets inside the habitable zones of M stars most likely do not build up dense atmospheres over long time periods, due to thermal and nonthermal atmospheric escape processes, geophysical difficulties related to plate tectonics (Lammer *et al.,* 2009), and surface weathering of $CO_2$.

Planets located around M and K stars could catastrophically outgas dense steam atmospheres during the solidification of their magma oceans (*e.g.,* Elkins-Tanton, 2012). Similar to G star planets, after about 1–2 Myr the water vapor then condenses (Hamano *et al.,* 2013; Lebrun *et al.,* 2013; Massol *et al.,* 2016; Salvador *et al.,* 2017), and a liquid ocean forms. $CO_2$ would then weather out of the atmosphere (*e.g.,* Walker *et al.,* 1981; Alt and Teagle, 1999; Lammer *et al.,* 2018, and references therein).

Lammer *et al.* (2007) and Airapetian *et al.* (2017b) suggested that nonthermal atmospheric ion escape caused by radiative forcing could incur a significant atmospheric loss rate due to the long-lasting high stellar EUV flux of M- and K-type stars. Figure 9b shows the response of the exobase level for an Earth-type nitrogen atmosphere in relation to the incident EUV flux. For young planets, the EUV-heated upper atmosphere exceeds the magnetopause levels, easily leading to massive nitrogen loss rates of 300 mbar/Myr for 10 $F_{\mathrm{EUV,Earth}}$ and much more for higher fluxes (Lichtenegger *et al.,* 2010). In the case of $CO_2$ atmospheres, $CO_2$ can be massively dissociated, but the products (oxygen, carbon) cannot accumulate due to efficient escape; thus an Earth-sized planet is not able to build up a dense atmosphere (Lammer *et al.,* 2007; Tian, 2009; Airapetian *et al.,* 2017b). Moreover, Airapetian *et al.* (2017b) found that the escape time of a 1 bar atmosphere on a terrestrial-type planet in the habitable zone of Proxima Cen b is expected to be about 10 Myr. In agreement with these results, a more recent study by Johnstone *et al.* (2019) found extreme hydrodynamic losses of Earth-like atmospheres in the habitable zones of very active stars, resulting in the complete evaporation of a modern Earth atmosphere in $\leq 0.1$ Myr. One can conclude that atmospheres of M and K star Earth-like habitable zone planets, which could maintain liquid water oceans on their surface, are unlikely to build up $N_2$-dominated atmospheres. Due to high thermal and nonthermal atmospheric escape rates, the remaining thin atmospheres will most likely be $CO_2$-dominated similar to present Mars, although further (model) studies are needed.

## 6. Implications for the Search for Life on Earth-like Exoplanets and Possible Detection Methods

The central issues regarding the existence of a potential Earth-like biosphere on a hypothetical ocean-surface environment of an extraterrestrial Earth-like planet are connected to the oxidation states of atmosphere and interior, the need for a fully oxidized surface and uppermost mantle, and the likely necessity of plate tectonics. Therefore, the buildup of a dense $N_2$-dominated atmosphere is strongly linked to the planetary oxygenation time, atmospheric $O_2$, and life-forms that are capable of denitrification (Zerkle and Mikhail, 2017; Zerkle *et al.,* 2017; Lammer *et al.,* 2018, and references therein).

Plate tectonics is a crucial factor for maintaining the activity of the carbon-silicate cycle over geological timescales (*e.g.,* Walker *et al.,* 1981; Kasting, 1993; McCammon, 2005; Southam *et al.,* 2015; Krissansen-Totton *et al.,* 2018a). The manner in which plate tectonics starts and operates and whether it is geophysically stable (or transient) over the planetary lifetime are however not fully understood (*e.g.,* Tackley, 2000; Bercovici, 2003; Bercovici and Ricard, 2003; van Hunen and Moyen, 2012; Gerya *et al.,* 2015; O'Neill *et al.,* 2016). Such feedbacks are likely necessary for determining the outgassing of $N_2$-dominated atmospheres, which is related to the origin of complex life and long-term habitability.

Water-rich Earth-like planets inside the habitable zone without both active plate tectonics and life-forms that are capable of denitrification most likely never build up dense secondary outgassed $N_2$-dominated atmospheres. One should keep in mind that on ocean worlds, whether life exists there or not (Noack *et al.,* 2016), the buildup of $CO_2$-dominated atmospheres is unlikely due to proposed destabilizing climate feedbacks (Kitzmann *et al.,* 2015), but we do not focus on such scenarios here. In the case of M- and K-type host stars, due to the stars' long-lasting active radiation and plasma environment, the atmospheres of Earth-like planets inside the habitable zones of these stars will experience high mass loss rates, which could also prevent the formation of dense secondary atmospheres.

Especially if the planet lacks a magnetosphere, thin atmospheres (surface partial pressures of a few millibar to a few tens of millibar) will not greatly protect the surface environment from the exposure to highly energetic cosmic rays (Brack *et al.,* 2010; Belisheva *et al.,* 2012; Grießmeier *et al.,* 2016). In that case, secondary radiation caused by particle showers in such a thin atmosphere will likely have global effects and may prevent life or sterilize the planet's surface (*e.g.,* Belisheva *et al.,* 1994; Belisheva and Popov, 1995; Belisheva and Emelin, 1998; Dar *et al.,* 1998; Belisheva and Gak, 2002; Smith and Scalo, 2004; Grießmeier *et al.,* 2005; Brack *et al.,* 2010; Pavlov *et al.,* 2012). In the case of an Earth-like planet, the effects of highly energetic particles on biological systems could be strongly reduced or negligible because life-forms would keep the atmosphere dense enough through denitrification such that high-energy particles are shielded from the surface in an efficient way.

Moreover, according to Catling *et al.* (2005), the rather long oxygenation time could preclude complex life on Earth-like planets orbiting early-type stars, which end their main sequence lives before sufficient oxygenation can occur. Conversely, Earth-like planets inside the habitable zones of solar-like G stars are potentially more favorable habitats for the evolution of complex life-forms.

To conclude, in accordance with our argumentation and in agreement with Stüeken *et al.* (2016a), we expect $N_2$ and $O_2$ as major constituents of terrestrial planetary atmospheres to be a geo-biosignature for a biosphere populated by highly developed life-forms. The bacterial by-product, $N_2O$, provides a similar indication (Muller, 2013).

Among the many instruments and space missions currently under development, PLATO (Rauer *et al.,* 2014) is in the best position for the detection of transiting Earth-sized planets orbiting in the habitable zone of G-type stars. Due to their transiting geometries and bright central host stars, the atmosphere of these planets can then be observed and characterized through multiwavelength transmission spectroscopy (*e.g.,* Seager *et al.,* 2000; Brown, 2001). The coronagraphs on board future space missions currently under development, such as HABEX (Mennesson *et al.,* 2016) and LUVOIR (Bolcar *et al.,* 2016), will have the capability to directly image low-mass planets in the habitable zone of G-type stars and directly measure their emission spectra. For transiting planets, future large missions may allow us to additionally obtain transmission spectra. However, these may not be able to probe the deepest atmospheric layers where most of the water resides, due to refraction (García Muñoz *et al.,* 2012; Misra *et al.,* 2014b). Fujii *et al.* (2018) provide a comprehensive review of future planned observations in a biosignature context.

In the previous sections, we showed that from our current knowledge of Earth's atmospheric evolution, it is possible to conclude that the detection of an $N_2$-dominated atmosphere presenting a strong component of $O_2$ and a negligible amount of $CO_2$, possibly accompanied by the presence of $O_3$, $H_2O$, $CH_4$, and $N_2O$, can decisively indicate the presence of an Earth-like habitat and therefore an aerobic biosphere (Airapetian *et al.,* 2017a). The possible detectability of an anoxic habitat, such as that of Earth during the Archean with a $CH_4$-rich atmosphere, is given by Arney *et al.* (2016) and Krissansen-Totton *et al.* (2018b). Oxygen and water molecules feature several transition bands ranging from the near-UV to the IR, some of them particularly strong, that can be used to detect and measure the abundance of those molecules. Similarly, $CO_2$ presents strong molecular transition bands in the IR, which can thus be used to detect and measure its abundance (*e.g.,* Rauer *et al.,* 2011; Bétrémieux and Kaltenegger, 2013; Hedelt *et al.,* 2013; Arney *et al.,* 2016), for example through transmission spectroscopy carried out with high-resolution spectrographs attached to the Extremely Large Telescope (ELT) (*e.g.,* de Kok *et al.,* 2013; Brogi *et al.,* 2014; Snellen *et al.,* 2017).

The detection of nitrogen is far more challenging. However, nitrogen oxides are deeply linked to biological and atmospheric processes (Muller, 2013). For instance, on Earth $N_2O$ would be efficiently depleted by photodissociation in the troposphere, if it were not protected by the ozone layer. $NO_2$ and $N_2O$ feature molecular transition bands in the blue optical region and at near-UV wavelengths, but their strength is significantly smaller than those of other molecules (*e.g.,* $O_2$, $O_3$) located at similar wavelengths (Bétrémieux and Kaltenegger, 2013), making their detection challenging. $N_2O$ has two further IR absorption bands (at about 4.5 and 7.8 μm), although these are generally also rather weak (Rauer *et al.,* 2011; Hedelt *et al.,* 2013). Pallé *et al.* (2009) showed that the IR absorption features of the $O_2 \cdot O_2$ and $O_2 \cdot N_2$ dimers at 1.26 μm are in principle detectable in the transmission spectrum of an Earth-like planet, assuming the spectral resolution and signal-to-noise ratio are high enough. Misra *et al.* (2014a) showed that the analysis of the dimer $O_2 \cdot O_2$ may lead to a measurement of the atmospheric $O_2$ pressure, which would be extremely valuable for the characterization of Earth-like planets. However, a similar study has not yet been carried out for the $O_2 \cdot N_2$ dimer, which may lead to the detection of nitrogen and, more importantly, to a measurement of the $N_2$ atmospheric abundance and pressure. Observationally, the $O_2 \cdot N_2$ dimer could be detected and measured from the ground using the ELTs.

The upper atmosphere of Earth is mostly composed of atomic hydrogen, nitrogen, and oxygen. Various processes, such as resonance scattering and charge exchange with the solar wind, lead to the formation of a number of emission lines of atomic H, N, and O, the strongest ones located between X-rays and optical wavelengths. These atoms, located in the upper atmosphere, would also appear in transmission spectra of transiting Earth-like planets. In this case, due to the low atmospheric density, the most favorable features are those in the far-UV (122–200 nm). The reason is that the relatively weak stellar far-UV fluxes would be partially compensated by the extended upper planetary atmosphere at these wavelengths. If strong enough, these emission and/or absorption features might be detectable, allowing to reveal indirectly the presence or absence of a given element in the atmosphere of an Earth-like exoplanet. To this end, these lines might be detectable by future large aperture multipurpose telescopes, such as LUVOIR, thanks to the unprecedented high far-UV sensitivity of the LUMOS (France *et al.,* 2017) and POLLUX (Bouret *et al.,* 2018) spectrographs.

Finally, an $N_2$-$O_2$ atmosphere is transparent for sunlight due to the oxidation of visible-light absorbers through $O_2$. This allows effective Rayleigh scattering on $O_2$ molecules leading to the famous ''blue planet'' appearance (Krissansen-Totton *et al.,* 2016b), which makes an Earth-like Rayleigh absorption feature in the visible consistent with an $N_2$-$O_2$ atmosphere a biosignature.

Given the great opportunity that the detection of atmospheric nitrogen compounds would provide for the identification of Earth-like habitats, it is important for future studies to address thoroughly the detectability of this species in the atmosphere of Earth-like planets and to establish what kind of information (such as detection alone, the abundances, pressures, etc.) a given method could provide. It is also important to note that it is crucial to study the detectability of these features for planets with atmospheric pressures and compositions slightly different from those of Earth and also orbiting stars different from the Sun.

## 7. Conclusion

There is a strong correlation between an $N_2$-dominated atmosphere and other constituents like $O_2$, $O_3$, and $H_2O$. Such dual detections constitute a biosignature for aerobic life. The latter is the vital contributor to maintain nitrogen-dominated atmospheres and drastically impact the composition of an Earth-like atmosphere via complex interactions. Plate tectonics remain another crucial factor, and the possible influence of life to its development is yet to be thoroughly investigated. Conversely, it is likely that life on Earth would have developed differently, if plate tectonic processes had not operated efficiently. Thus, the detection of atmospheric nitrogen would indicate a tectonically active world (''geo-signature''), whereas $N_2$ and $O_2$ in combination represent a geo-biosignature, while we do not rule out that an anaerobic biosphere is present without maintaining such conditions.

If such an interplay of atmosphere, lithosphere, and biosphere providing a base for highly developed life is rare, the atmospheres of most terrestrial planets in the habitable zones would be $CO_2$-dominated. This molecule presents a number of absorption bands in the IR, making it detectable from the ground with high-resolution spectrographs attached to the ELTs. Our hypothesis could therefore be proven by characterizing the atmosphere of Earth-sized planets detected by TESS and PLATO. The next step could then be the quantification of the habitability occurrence rate, which would require the detection of nitrogen, thus the use of the next generation ground- and space-based telescopes (*i.e.,* ELTs, LUVOIR).

The buildup of any substantial amount of nitrogen might be still more difficult around M and also K stars, due to both different geodynamics and their long-lasting phase of strong EUV irradiation leading to severe escape.

Identifying nitrogen and oxygen as primary ingredients of an exoplanet's atmosphere is not only an indication for an oxidized lithosphere and a tectonically active world; it also indicates the existence of an aerobic biosphere.

## Appendix

To give an overview on the estimations of nitrogen exchange rates within Earth's nitrogen cycle of today, some tables (Tables A1, A2, A3, and A4) are included here. These tables contain the respective outgoing rates of the reservoirs' atmosphere (with atmosphere fixed), soil (with land biota),

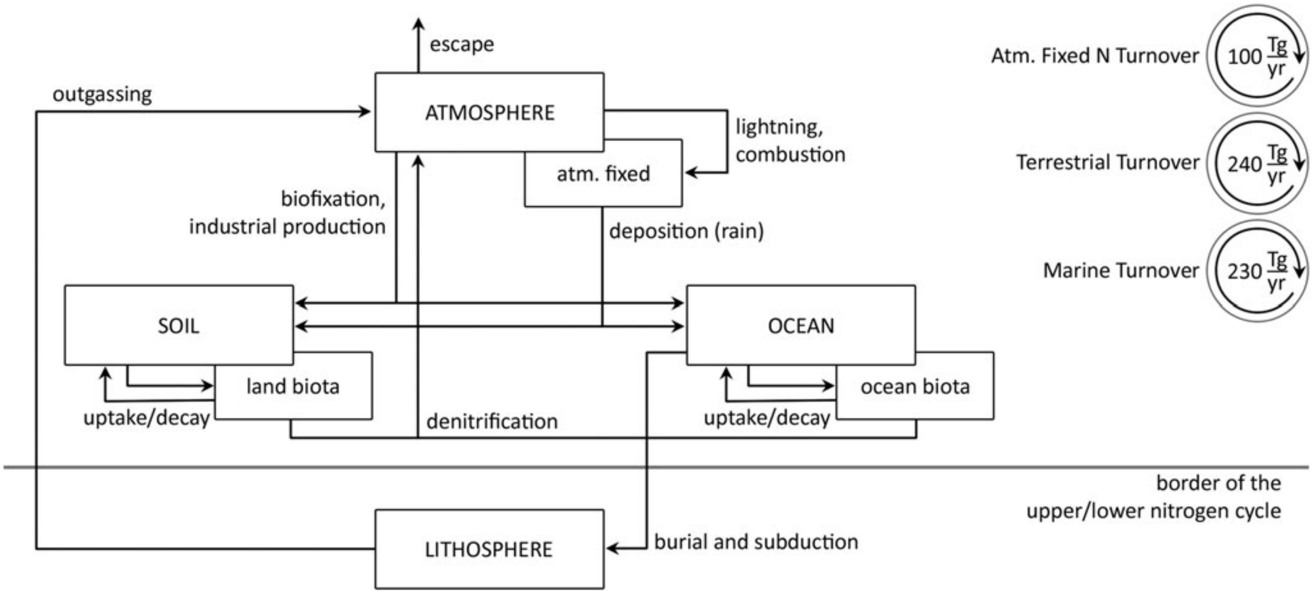


**FIG. A1.** Simplification of Earth's present-day nitrogen cycle. There are four main reservoirs (atmosphere, soil, ocean, and lithosphere), which build the basic structure for the different rates in Tables A1, A2, A3, and A4. The turnover rates are according to Fowler *et al.* (2013).

TABLE A1. SIGNIFICANT NITROGEN DEPLETION RATES FROM THE ATMOSPHERE IN (TG N)/YR

| *Process* | *Receiving reservoir* | *Jaffe (1992)* | *Jacob (1999)* | *Galloway (2003)*[a] | *Fowler* et al. *(2013)* | *Diverse sources* |
|---|---|---|---|---|---|---|
| atmosphere | | | | | | |
| industrial production | soil, l. bio. | 40 (40) | 80 (80) | 79 (79) | 120 (120) | 60 (60)[b] |
| share of fertilizer prod. | l. bio. | | 80 (80) | | 100 (100) | |
| fossil fuel combustion | atm. f. | 20 (20) | | 23 (23) | 30 (30) | |
| biomass burning (fixation)[c] | atm. f. | 12 (10)[d] | 25 (-)[e] | | | |
| biofixation (land) | l. bio. | 150 (-) | 160 (-) | 146 (41) | 118 (60) | 110 (-)[f] |
| agricultural percentage | l. bio. | | | 41 (41) | 60 (60) | |
| naturogenic percentage | l. bio. | | | 105 (0) | 58 (0) | |
| biofixation (ocean) | o. bio. | 40 (0) | 20 (-) | 68 (0) | 140 (0) | 40 (-)[f] |
| lightning | atm. f. | 5 (0) | 5 (0)[e] | 4 (0) | 5 (0)[g] | 3 (0)[f] |
| loss to the stratosphere | - | 9 (0) | | | | 9 (0)[f] |
| atmosphere: fixed N | | | | | | |
| deposition (land) | soil | 125 (0) | 80 (0) | 74 (0) | 74 (0)[g] | |
| deposition (ocean) | ocean | 34 (0) | 30 (0) | 30 (0) | 31 (0)[g] | 76 (0)[h] |
| Total Rate | | | | | | |
| to soil/land biota | | 315 | 320 | 299 | 312 | |
| to ocean/ocean biota | | 74 | 50 | 98 | 171 | |
| to lithosphere | | 0 | 0 | 0 | 0 | |

[a]Mean of values given by Galloway *et al.* (1995) and Schlesinger (1997), summarized in Galloway (2003, S. 567).
[b]Rosswall (1983).
[c]Here, biomass burning represents primarily nitrogen fixation of atmospheric dinitrogen, similar to fossil fuel combustion. In some models, biomass burning describes volatilization of fuels' organic nitrogen during the burning process. Therefore, there is also biomass burning in the land biota outgoing flux table.
[d]The anthropogenic percentage is estimated, because there are only explanations and no reliable values given in the original description.
[e]Originally, there is a flux ''combustion and lightning'' of 30 (Tg N)/yr, whereby lightning is declared as a minor part. The splitting into biomass burning (including fossil fuel combustion) and lightning is merely estimated.
[f]Stedman and Shetter (1983).
[g]In the original study, lightning products are declared as directly washed out into soil. Therefore, it is proportionally added to deposition rates in this table.
[h]Voss *et al.* (2013).

TABLE A2. SIGNIFICANT NITROGEN DEPLETION RATES FROM THE SOIL IN (TG N)/YR

| *Process* | *Receiving reservoir* | *Jaffe (1992)* | *Jacob (1999)* | *Galloway (2003)*[a] | *Fowler* et al. *(2013)* | *Diverse sources* |
|---|---|---|---|---|---|---|
| soil | | | | | | |
| leaching and river runoff | ocean | 34 (0) | 40 (0) | 76 (0) | 80 (0) | |
| groundwater percentage | ocean | | | | 4 (0) | |
| riverine flux[b] | ocean | | | | 40–70 (0) | |
| biotic uptake | l. bio. | | 2300 (2300) | | | |
| land biota | | | | | | |
| biomass burning (volit.)[c] | atm. f. | | | 19 (19) | 5 (4) | |
| soil/agriculture emission[d] | atm. f. | 130 (>5) | 80 (-) | 60 (-) | 65 (41) | |
| $NH_3$ percentage | atm. f. | 122 (-) | | 60 (-) | 60 (40) | |
| NO percentage | atm. f. | 15 (0) | | | 5 (1) | |
| burial/decay | soil | | 2500 (2500) | | | |
| denitrification | atm. | 147 (0) | 130 (0) | 177 (0) | 113 (7) | 125 (-)[e] |
| $N_2O$ percentage | atm. | | | 10 (0) | 13 (7) | |
| Total Rate | | | | | | |
| to atmosphere/atm. fixed | | 284 | 210 | 256 | 183 | |
| to ocean/ocean biota | | 34 | 40 | 76 | 80 | |
| to lithosphere | | 0 | 0 | 0 | 0 | |

[a]Mean of values given by Galloway *et al.* (1995) and Schlesinger (1997), summarized in Galloway *et al.* (2003, S. 567).
[b]Fish landing is often not mentioned or, if the level of detail is high enough, already subtracted from river runoff. Voss *et al.* (2013) estimated a flux of 3.7 (Tg N)/yr, which would be clearly large enough to be considerable.
[c]This represents primarily the nitrogen within the fuel which is volatilized; thus, in this case, this flux is not a source for fixed nitrogen. In some models the biomass burning flux describes a fixing process of atmospheric $N_2$, similar to fossil fuel combustion. Therefore, there is also biomass burning in the atmospheric outgoing flux table.
[d]Denitrification rates are indeed also a form of soil emission. Here they are listed separately for a better understanding.
[e]Stedman and Shetter (1983).

Table A3. Significant Nitrogen Depletion Rates from the Ocean in (Tg N)/yr

| *Process* | *Receiving reservoir* | *Jaffe (1992)* | *Jacob (1999)* | *Galloway (2003)*[a] | *Fowler* et al. *(2013)* | *Diverse sources* |
|---|---|---|---|---|---|---|
| ocean | | | | | | |
| ocean emission | atm., atm. f. | | ≈ 0 (0) | 13 (0) | 14.5 (0) | |
| $NH_3$ percentage | atm. f. | | | 13 (0) | 9 (0)[b] | |
| $N_2O$ percentage | atm. | | | | 5.5 (3) | |
| biotic uptake | o. bio. | | 1600 (1600) | | | |
| ocean biota | | | | | | |
| denitrification | atm. | 30 (0) | 100 (0) | 141 (0) | 100–280 (0) | 31 (-)[c] |
| $N_2O$ percentage | atm. | | | 3 (0) | 5.5 (0) | |
| burial/decay | ocean | | 1600 (0) | | | |
| burial and subsidence | lith. | 14 (0)[d] | 10 (0) | ∼0 (0) | 20 (0) | 1.3[e] |
| Total Rate | | | | | | |
| to atmosphere/atm. fixed | | 30 | 100 | 154 | 114.5–294.5 | |
| to soil/land biota | | 0 | 0 | 0 | 0 | |
| to lithosphere | | 14 | 10 | 0 | 20 | |

[a]Mean of values given by Galloway *et al.* (1995) and Schlesinger (1997), summarized in Galloway (2003, S. 567).
[b]This value of $NH_3$ percentage also contains volcanic emissions.
[c]Stedman and Shetter (1983).
[d]While most studies lack any entry of weathering processes back from seafloor to the ocean, this study has such a flux. Here, the net value of subducted nitrogen is given.
[e]Hilton *et al.* (2002).



Table A4. Significant Nitrogen Depletion Rates from the Lithosphere in (Tg N)/yr

| *Process* | *Receiving reservoir* | *Jaffe (1992)* | *Hilton* et al. *(2002)* | *Sano* et al. *(2001)* | *Catling and Kasting (2017)* | *Diverse sources* |
|---|---|---|---|---|---|---|
| lithosphere | | | | | | |
| outgassing: MORs | atm. | 1.000 | 0.0280 | 0.0616 | 0.1064[a] | 0.0616[b] |
| outgassing: island arcs | atm. | | 0.5546 | 0.0179 | 1.4706 | 0.9804[c] |
| recycled percentage | atm. | | | 0.0126 | 0.4202 | |
| outgassing: BABs | atm. | | | 0.0157 | | |
| recycled percentage | atm. | | | 0.0067 | | |
| seafloor weathering[d] | ocean | 5.000 | | | | 14.000[e] |
| lower mantle | | | | | | |
| hotspot volcanic action | atm. | | | 0.0001 | 0.8403 | |
| Total Rate | | | | | | |
| to atmosphere/atm. fixed | | 1.000 | 0.5826 | 0.0953 | 2.4173 | |
| to soil/land biota | | 0 | 0 | 0 | 0 | |
| to oceanic/ocean biota | | 5.000 | 0 | 0 | 0 | |

[a]Taken from Marty *et al.* (2013).
[b]Marty (1995).
[c]Fischer (2008).
[d]Some studies lack this entry and take the ''burial and subsidence'' from ocean to lithosphere as net flux.
[e]Stedman and Shetter (1983).

ocean (with ocean biota), and lithosphere. A visualization of this simplified description is given in Fig. A1. All total rates, given in the lower part of the tables, refer to the exchanges between the four combined complexes, readily identifiable in the graphic.

Note that the yearly turnovers (see also Fig. A1) are high in respect to the total global nitrogen exchange rates between the different reservoirs, which means that nitrogen is not only processed in a global way but rather also efficiently (re)cycled in the smaller subsystems.

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## Author Disclosure Statement

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**Abbreviations**

anammox = anaerobic ammonium oxidation
ELT = Extremely Large Telescope
GOE = Great Oxidation Event