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Co-Evolution of Atmospheres, Life, and Climate

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Abstract

After Earth’s origin, our host star, the Sun, was shining 20–25% less brightly than today. Without greenhouse-like conditions to warm the atmosphere, our early planet would have been an ice ball, and life may never have evolved. But life did evolve, which indicates that greenhouse gases must have been present on early Earth to warm the planet. Evidence from the geological record indicates an abundance of the greenhouse gas CO2. CH4 was probably present as well; and, in this regard, methanogenic bacteria, which belong to a diverse group of anaerobic prokaryotes that ferment CO2 plus H2 to CH4, may have contributed to modification of the early atmosphere. Molecular oxygen was not present, as is indicated by the study of rocks from that era, which contain iron carbonate rather than iron oxide. Multicellular organisms originated as cells within colonies that became increasingly specialized. The development of photosynthesis allowed the Sun’s energy to be harvested directly by life-forms. The resultant oxygen accumulated in the atmosphere and formed the ozone layer in the upper atmosphere. Aided by the absorption of harmful UV radiation in the ozone layer, life colonized Earth’s surface. Our own planet is a very good example of how life-forms modified the atmosphere over the planets’ lifetime. We show that these facts have to be taken into account when we discover and characterize atmospheres of Earth-like exoplanets. If life has originated and evolved on a planet, then it should be expected that a strong co-evolution occurred between life and the atmosphere, the result of which is the planet’s climate. Key Words: Early Earth—Biomarker—Atmospheres—Climate—Exoplanets. Astrobiology 10, 77–88.

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1. How Life Has Affected Earth’s Atmosphere

To estimate the occurrence of terrestrial exoplanets and maximize the chance of finding them, it is crucial to understand the formation of planetary systems in general and of terrestrial planets in particular. A reliable formation theory should not only explain the Solar System, with small terrestrial planets within a few AU and gas giants farther out, but also the newly discovered planetary systems with close-in giant planets. Regarding the presently known exoplanets, it should be stressed that our current knowledge is strongly dependent upon the sensitivity limits of the current detection techniques (mainly the radial velocity method). With time and improved detection methods, the diversity of planets and orbits in exoplanetary systems will definitely increase and help to constrain the formation theory further.

Nitrogen on Earth was outgassed during the first hundred million years. Therefore, the atmospheric pressure was at least 0.8 bar in Earth’s prebiotic atmosphere. If climate regulation via the carbonate-silicate cycle is assumed (Walker, 1977; Walker et al., 1981), then the level of CO₂ is determined to a first approximation by the solar luminosity.

- Due to the faint luminosity of the early Sun (e.g., Gough, 1981; Baraffe et al., 1998), about 200–300 mbar of CO₂ would have been necessary to ensure a mean surface temperature above 273 K (Kasting et al., 1993).

Molecular hydrogen was likely the third main component of Earth’s prebiotic atmosphere; in an enhanced presence of CO₂ and if large amounts of hydrogen were absent in the upper atmosphere, the exosphere may have been relatively cool, which could have resulted in low escape rates of atomic hydrogen (Tian et al., 2005). Hydrogen that was released by volcanoes but not efficiently lost to space must have accumulated to levels of the order of 200 mbar (Tian et al., 2005). As water was present on Earth before 4.4 Gyr, water vapor was also an important constituent of the lower atmosphere. Other atmospheric species that may have been present at this time include CO and sulfur-bearing species like H₂S released by volcanoes and possibly methane produced abiotically in hydrothermal vents.

1.1. A rise in methane?

Among the most primitive archaea found in the tree of life, as shown in Fig. 1, are the methanogens, some of which are autotrophic (consuming CO₂ and H₂) and others heterotrophic (consuming organic molecules). Methane is a trace gas in the present Earth atmosphere (about 2 ppm), and its origin is biological except for a small fraction produced in hydrothermal systems.

- Methanogens existed almost certainly during the Archean and the Neoproterozoic, when the atmosphere was still anoxic (before 2.3 Gyr).

If we assume a biogenic release equal to the present day, the level of methane would have reached 100–1000 present atmospheric level (PAL) in the absence of atmospheric O₂ (Pavlov et al., 2000). As today’s methanogens can only grow in very limited environments where O₂ is absent and H₂ or organics are present, the production of methane by the biosphere was probably much higher in the early anaerobic environment. Thus, very high levels of methane can be inferred, which lasted for more than 1 Gyr, between the emergence of methanogens (probably earlier than 3.4 Gyr) and the rise of O₂ (2.3 Gyr).

- Such high levels of CH₄ would have had a strong impact on climate and geochemical cycles. Methane is a very efficient greenhouse gas, and levels higher than 100 PAL would potentially have been enough to warm the surface above 0°C (Pavlov et al., 2000), which implies that climate is no longer regulated by the carbonate-silicate cycle. The level of CO₂ could potentially have been extremely low if methane became the main greenhouse gas, and this seems to be confirmed by the studies of paleosols from the Late Archean and Neoproterozoic, in which no trace of carbonates were found (Rye et al., 1995; Hessler et al., 2004). Note that this does not take the effect of hazes into account. In the early atmosphere, the haze expected from CH₄ photolysis was probably weak if the CH₄/CO₂ ratio did not exceed unity. If the ratio had exceeded unity, an organic haze would have formed (Pavlov et al., 2003) such that it would have potentially cooled the atmosphere and regulated the greenhouse effect. Another important consequence of high levels of CH₄ is the transport of hydrogen, which would have dissociated from methane by high extreme UV radiation of the young Sun to the upper atmosphere and led to a much higher escape rate of hydrogen to space.

Thus, it might be possible that biological methanogens contributed to the oxidation of the atmosphere and lithosphere and enhanced the loss of H₂, making possible, later, the rise of oxygen (Catling et al., 2001).

1.2. The buildup of O₂

Geological records have revealed the chemical action of free oxygen after about 2.3 Gyr ago (Bekker et al., 2004), except for some deposits from the deep ocean that remained anoxic for a few hundred million years or more (Rouxiel et al., 2005).

- It seems that the buildup of atmospheric O₂ occurred at least 400 Myr after the emergence of oxygen-producing bacteria capable of oxygenic photosynthesis (Fig. 2).

Indeed, 2.7 Gyr old molecular fossils are interpreted as the remains of primitive cyanobacteria and eukaryotes, which are producers and consumers of O₂, respectively (Brocks et al., 1999). Several reasons could explain this delay. First, the budget reaction of oxygenic photosynthesis also works in the reverse direction, since respiration and oxidation of organic sediments consume oxygen.

- Thus, the buildup of atmospheric O₂ requires the burial of the organics produced by photosynthesis.

This occurs today at a rate of 589 Tg O₂/year (Catling and Claire, 2005), which means that the net release of the present O₂ atmospheric content (10²³ g O₂) takes about 2 Myr (this is about 1000 times slower than the production of O₂ by photosynthesis). This rate is balanced by the oxidation of rocks, old sediments, and volcanic gases. The oxidation sinks for O₂ may have been much more efficient on early Earth, partly
due to the presence of large amounts of reduced iron in the ocean and the crust (Walker, 1977).

- In the absence of efficient organic burial, O$_2$ would not build up.

Some tectonic processes may have favored the burial of reduced carbon and allowed the rise of O$_2$ by about 2 Gyr ago (Des Marais et al., 1993). Another hypothesis has already been mentioned and is linked with the slow oxidation of Earth through the escape of hydrogen to space: in other words,

\[ 2\text{H}_2\text{O} + \text{CO}_2 + \text{hv} \rightarrow \text{CH}_2\text{O} + \text{O}_2 + \text{H}_2\text{O} \]

![FIG. 1.](image1.png)  
**FIG. 1.** Tree of life: in black are indicated some methanogens that are among the most primitive life-forms known (courtesy of N. Pace).

![FIG. 2.](image2.png)  
**FIG. 2.** Illustration of reactions that result in a release of O$_2$ in Earth’s atmosphere. Color images available online at www.liebertonline.com/ast.
the Earth had to be depleted of a lot of hydrogen before an oxygen atmosphere could occur.

There might also be a climatic reason for the delay between the emergence of O₂ producers and the rise of O₂. CH₄ has a very short photochemical lifetime in an O₂-rich atmosphere, which means that a consequence of a buildup of O₂ is a decrease of the CH₄ atmospheric abundance and, thus, a fall of the mean surface temperature that could lead to a global freezing event.

Therefore, in a biosphere where CH₄ and O₂ producers both exist, the solar luminosity might be a strong constraint on the timing of the oxygenation (Selsis, 2002).

All these constraints on the buildup of an O₂-rich atmosphere are extremely important for astrobiological considerations, as some authors argue that complex multicellular life can only develop in an oxic environment (e.g., Catling et al., 2005).

Geological records have provided us with only qualitative information about the presence or absence of oxygen in the atmosphere. After the rise of O₂ and until the end of the Precambrian (about 550 Myr ago), it can only be inferred that the level of O₂ was above about 1% PAL (0.2% in abundance). Models based on the chemical and isotopic composition of sedimentary rocks of the Phanerozoic (from 550 Myr ago to now) allow us to trace back the evolution of the level of O₂ and show that it has varied roughly between 0.7 and 1.8 PAL (Berner et al., 2003).

The highest oxygen level (nearly twice that of today, which implies an atmospheric pressure 15% higher) is found to have occurred during the Permo-Carboniferous.

The principal cause of this enhanced level was the rise of large vascular land plants and the consequent increased global burial of organic matter. Higher levels of O₂ are consistent with the presence of Permo-Carboniferous giant insects.

1.3. The rise of the ozone layer

Ozone (O₃) is produced by only one reaction: O + O₂ + M → O₃ + M, where M is any compound (this is called a three-body or association reaction) and atomic oxygen comes from the photolysis of O₂. On the other hand, O₃ is destroyed by photolysis and many trace compounds in the atmosphere (HOₓ, NOₓ, ClOₓ, ...).

Therefore, the amount of O₃ in the atmosphere depends on the level of O₂ but also on the abundance of these trace gases on which we do not have enough information to infer the level of O₃ in the Precambrian.

The variation of O₂ alone during the last 550 Myr would not have changed significantly the level of O₃, as O₃ has only a weak dependency on the O₂ level (Léger et al., 1993; Segura et al., 2003).

The abundance of O₃ was more certainly affected by changes in the content of trace gases. We do not know for sure whether, between the rise of O₂ and the beginning of the Phanerozoic, O₃ provided a UV shield for land life, but it can be inferred that it was present when the first lichens colonized the lands during the Ordovician (500–425 Myr ago).

2. Stellar Radiation and Climate: Implications for Atmospheric Biomarkers*

It is well known from satellite observations and the output of coupled chemistry-climate models on Earth that important physical factors like atmospheric temperature and solar radiation affect atmospheric biomarker molecule concentrations over diurnal and seasonal timescales.

Since it is expected that a terrestrial exoplanet-finding mission will discover terrestrial exoplanets for various stellar spectral types and stellar evolution phases, how different radiation inputs and climate feedbacks can affect biomarker signals must be studied.

As a first step, changes to biomarkers in Earth’s atmosphere in response to variations related to orbital parameters, climate feedbacks, and the radiation and particle environment of the Sun or stars or both can be studied with the use of theoretical climate models (Fig. 3).

2.1. Ozone (O₃)

Tropospheric O₃ makes up about 10% of the overhead column content in the terrestrial atmosphere. In the lower troposphere (0–8 km), O₃ is formed when volatile organic compounds such as CH₄ are oxidized in the presence of NOₓ (see overview in Crutzen, 1988), and it is destroyed by surface deposition. In the mid- to upper troposphere (8–18 km), stratospheric-tropospheric exchange affects O₃ concentrations. Here, stratospheric air may fold down into the troposphere and release O₃-rich air. Stratospheric O₃ makes up about 90% of the O₃ layer that forms when O₂ is photolyzed (<242 nm) into O, which then reacts with O₂ to form O₃.

Why does an O₃ layer form at a specific altitude?

In the lower atmosphere, there is little O₃ because UV radiation is weak; in the upper atmosphere, there is little O₂ because there is little O₂. Figure 4 shows that the trade-off between UV and O₂ availability with altitude leads to a sharply defined O₃ maximum in the tropical stratosphere at 10 mbar (30 km), which travels each year across the equator toward the summer hemisphere where photolysis rates are higher.

In the lower stratosphere (18–25 km, 100–50 mbar), chemical timescales that affect O₃ are long compared with dynamical timescales. Thus, O₃ behaves as a quasi-inert tracer of dynamical motion in that it is quasi-horizontal along isentropic (constant entropy) surfaces with typical stratospheric horizontal and vertical diffusion coefficients of 1000 and 0.015 m² s⁻¹, respectively (e.g., Waugh et al., 1997).

In the upper stratosphere (35–45 km, 5–1 mbar), O₃ is controlled mainly by chemistry. The main source is O₂ + O + M → O₃ + M, whereas important sinks are O + O₃ → 2O₂ and O₃ + hv (<320 nm) → O + O₂. These reactions were first discussed in depth by Chapman (1930) and are usually referred to as Chapman chemistry.

On Earth, O₃ is formed in the tropics via Chapman chemistry and is then transported slowly (over several months) to mid- and high latitudes.

*The term biomarker is used here to mean detectable atmospheric species or set of species whose presence at significant abundance strongly suggests a biological origin.
Chapman chemistry alone would produce more than twice as much O₃ as is measured. To explain the discrepancy, catalytic cycles that destroy O₃ were proposed:

\[
\begin{align*}
X + O_3 &\rightarrow XO + O_2 \\
XO + O &\rightarrow X + O_2
\end{align*}
\]

Overall : \(O_3 + O \rightarrow 2O_2\)

where X can be OH (Bates and Nicolet, 1950), NO (Crutzen, 1970), and Cl (Molina and Rowland, 1974). The cycles are referred to as HOx, NOx, and ClOx cycles. Stratospheric HOx comes, for example, from H₂O degradation, NOx from N₂O photolysis, and ClOx from man-made chlorofluorocarbons. HOx cycles are generally important in the tropical lower stratosphere, NOx in the middle, and ClOx in the upper stratosphere (e.g., Lary, 1997, and references therein).

- Stratospheric O₃ features a natural cycle with around 20% more column O₃ in spring than in autumn.

The spring maximum is associated with less photolytic O₃ loss over the preceding winter. At polar latitudes, the natural cycle is opposed by the O₃ hole that forms via chemical processes in spring with typically 30–60% loss in the column. Over short timescales (days to weeks), the O₃ column in mid- to high latitudes is affected by atmospheric dynamics (Staehelin, 1998).

In the mesosphere (50–85 km), intense UV radiation leads to a diurnal cycle with daytime conversion of O₃ to O³P. Observations by Zommerfelds et al. (1989) suggest a factor of 3 variation in O₃ at 65 km and a factor of 6 variation at 74 km. HOx cycles are an important sink for mesospheric O₃ (Summers et al., 1996).

2.2. Water (H₂O)

On Earth, the vast majority of atmospheric H₂O resides in the troposphere.

- The region around the tropopause acts as a cold trap that prevents most H₂O from reaching the stratosphere.

![ Observed O₃ concentration (parts per million by volume) shown as a function of altitude. Data represent the mean of 11 Januaries from 1992 to 2002, data level 2 version 19 measured by the Halogen Occultation Experiment aboard the Upper Atmosphere Research Satellite (Russell et al., 1993). ](image)
Figure 5 shows the H$_2$O concentration, as does Fig. 4 for O$_3$ as a function of zonal-mean height. Gettelman et al. (2000) reviewed processes that regulate the entry of H$_2$O from the troposphere into the stratosphere. Strong convective cloud events in the tropics achieve this if they penetrate the lower stratosphere. Methane oxidation is an important source of stratospheric H$_2$O and is initiated by reaction with hydroxyl (OH): CH$_4$ + OH $\rightarrow$ CH$_3$ + H$_2$O.

Mesospheric H$_2$O features an annual cycle with amplitude of ~20% and maximum in summer linked with stronger upward transport of damp air (Jackson et al., 1998).

### 2.3. Methane (CH$_4$)

On Earth, between 80–90% of CH$_4$ resides in the troposphere, where it is well mixed. Figure 6 shows CH$_4$ concentration as a function of zonal-mean height. During summer, when CH$_4$ oxidation is faster, the total column values are 5–10% lower than in winter. CH$_4$ is removed in the troposphere and stratosphere by reaction with the hydroxyl (OH) radical. This is a major source of water in the stratosphere.

- About one-third of CH$_4$, that is, $225 \times 10^{12}$ g/year (225 Tg) of CH$_4$ emissions arise naturally at the surface via, for example, geological activity (Etiopie and Klusman, 2002) or methanogenic bacteria under anaerobic conditions (wetlands and oceans) (Intergovernmental Panel on Climate Change, IPCC, 2001; Krüger et al., 2001).  
- The remaining two-thirds arise from human activity (industry and agriculture).  
- Stratospheric CH$_4$ is rather inert, with a typical lifetime of 5–10 years, so it acts as a tracer of dynamical air motions.

This can be seen in Fig. 6, which shows contours curving upward (rising air) in the tropics and downward (sinking air) toward the pole. This is the so-called equator-to-pole circulation of the Earth, which will be discussed later. Mesospheric CH$_4$ is low due to stratospheric oxidation.

### 2.4. Nitrous oxide (N$_2$O)

Like CH$_4$, N$_2$O is most abundant in the troposphere. It is extremely inert with a lifetime of around 150 years and, hence, is a good indicator of dynamical motions.

- $7-14 \times 10^{12}$ g/year N$_2$O are emitted into the atmosphere (Oonk and Kroeze, 1998), mainly via denitrifying bacteria.

In the stratosphere, about 95% N$_2$O is removed via photolysis in the stratosphere. The remaining 5% reacts with O$^1$D to form NO.

- A breakdown of N$_2$O contributes to O$_3$ destruction via NO$_x$ cycles.

Little N$_2$O survives into the mesosphere, where concentrations are about 500 times less than they are in the stratosphere.

### 2.5. Atmospheric dynamics and temperature

On Earth, the total O$_3$ column is sensitive to atmospheric dynamics because a large amount of O$_3$ resides between 18–25 km, where chemical loss is slow. Other biomarkers occur mainly in the troposphere, where they are well mixed, so their column values are less sensitive to dynamical influence.

- Enhanced solar heating in the tropics coupled with Earth’s rotation sets up an equator-to-pole flow called world circulation, meridional circulation, or Brewer-Dobson (Brewer, 1949) circulation (Holton, 2004).

On Earth, in a 10-year cycle, air enters the lower stratosphere in the tropics, travels up into the summer mesosphere, then back across the equator into the winter hemisphere, moving poleward and downward. The circulation is stimulated by atmospheric waves (Haynes, 1991), for example, gravity waves that can form when air flows over mountains or planetary

![Observed H$_2$O (ppmv) in January](image)
waves which form via conservation of potential vortices when air moves in the north-south plane on a rotating globe.

Figure 7 (left) shows zonal-mean temperature in Kelvin as a function of altitude. Up to 100 mbar air cools due to adiabatic expansion. Above that height, radiative heating, mainly from O3, leads to a temperature inversion and marks the start of the stratosphere. Between 1–0.1 mbar, this heating subsides, and cooling with height marks the start of the mesosphere.

3. Implications for Terrestrial Exoplanets

Earth’s climate is nonlinear with complex feedbacks. It is therefore challenging for current climate models to reproduce accurately, for example, the O₃ response to climate change over the past 20 years (see the IPCC Third Assessment Report on Climate Change, 2001, for an overview). Several groups have investigated Earth’s atmospheric evolution (Pavlov et al., 2000; Kasting and Catling, 2003) from reducing (i.e., non-oxidizing) atmospheres for which differing levels of CH₄ and CO₂ are assumed to the present-day atmosphere. Spectral modes of these evolution scenarios show different detectable features over Earth’s geological history in low resolution (Kaltenegger et al., 2007).

Ozone in the troposphere: sensitivity computational model runs for varying solar flux as well as CH₄, O₂, and NOₓ concentrations appropriate to the Proterozoic period of early Earth indicated that the tropospheric O₃ column could sometimes constitute appreciably more than today’s 10% of the total column (Grenfell et al., 2006). The additional O₃ was produced via the photochemical smog mechanism, in which CH₄ oxidation is catalyzed by NOₓ. The mechanism therefore favors terrestrial exoplanets with:

- abundant CH₄ from volcanoes, methanogens, or both;
- abundant NOₓ (from lightning and the action of cosmic rays on N₂/O₂ atmospheres).

Ozone photolysis effect: For Earth, the standard stratospheric Chapman chemistry analysis assumes both a rapid interconversion of O and O₂, and O in a steady state so that rate of O production equals rate of O loss, \( j(O₂) = k(O)(O₃) \), \( (O₃) = j(O₂)/(O)k \), where \( j \) and \( k \) are photolysis and reaction coefficients, respectively.

- For terrestrial exoplanets, these assumptions may not apply because the rate of O production and O loss depend, for example, on temperature and UV radiation; therefore, one has to apply in first steps a simpler approach.

The reaction O + O₃ \( \rightarrow \) 2O₂ quickly slows at low temperatures; therefore, one can assume a cold case, in which this reaction can be neglected. In such a case, O₃ is destroyed directly by \( hν < 320 \text{ nm} \) but is formed when O₂ dissociates at \( hν < 242 \text{ nm} \) (UVC). Therefore, under such conditions, an interesting quantity is the ratio, \( R = \frac{\text{UVB (280–315 nm)}}{\text{UVC (100–280 nm)}} \).

- If, on a terrestrial exoplanet, the atmospheric radiative transport differs potentially from Earth-like conditions, then regions that have small \( R \) values would experience weak O₃ loss (from direct O₃ photolysis in the UVB) but strong O₃ formation (from O₂ photolysis hence O₃ formation in the UVC).

At the top of the atmosphere, \( R \) is:

- \( R = 2.31 \) (Sun), \( R = 2.98 \) (K2V), and \( R = 0.92 \) (F2V) stars (Segura et al., 2003).

More studies are required to explore this theme further and establish where, or if, such effects can be valid.
Ozone temperature effect: That O$_3$ features a negative correlation with temperature has long been recognized (WMO, 1998). This behavior arises because the O$_3$ sink, O + O$_3$ → 2O$_2$, speeds up considerably as temperature increases. The temperature dependency can be seen from the rate constant of the reaction, $k$, where $k = 8.0 \times 10^{-12} \exp(-2060/T)$ (Sander et al., 2003). Substituting $T = 200, 250, 300$ K implies $k = (2.7, 21.1, \text{ and } 83.4) \times 10^{-16}$ molecules$^{-1}$ cm$^3$ s$^{-1}$, respectively, that is,

- It can be expected that a large increase in the O$_3$ sink occurs as $T$ increases.

This result is relevant to warm or hot exoplanets, for example, close to the inner edge of the habitable zone (HZ) or with strong greenhouse warming, or both.

Ozone and NO$_x$: Exoplanets in the HZ with M-dwarf hosts may have weak magnetospheres and, therefore, higher levels of cosmic ray bombardment. Grießmeier et al. (2005) suggested that the percent of cosmic rays that reach such a planet’s surface be a factor of 2–10 greater, compared with Earth, assuming the two worlds have similar surface areas.

- Enhanced cosmic ray events imply increased atmospheric NO$_x$ loadings because the cosmic ray particles can lead to ionization of N$_2$ (Siskind et al., 1997).
- Such events on Earth typically lead to a 50–100% increase in NO$_x$ in the upper stratosphere together with 10–30% O$_3$ loss (Jackman et al., 2000; Quack et al., 2001; Sinnhuber et al., 2003).

The amount of total O$_3$ column loss depends on how easily NO$_x$ can propagate down into the mid-stratosphere, where O$_3$ is most abundant.

- In such a scenario, destruction via HO$_x$ cycles would then likely destroy most of the O$_3$ layer.

In general, this mechanism suggests that a temperature increase at the surface leads to faster evaporation and, hence, higher atmospheric humidity. The effect is difficult to quantify in climate models due to opposing mechanisms (e.g., more H$_2$O leads to more clouds, which can produce a cooling effect) and interfering processes (e.g., stratospheric H$_2$O also comes from CH$_4$ oxidation, the cold trap temperature is influenced by other factors) (IPCC, 2001). One can anticipate that ocean-world (Léger et al., 2003) exoplanets are potentially most vulnerable to such a mechanism.

In addition to forming NO$_x$, cosmic rays may also lead to atmospheric HO$_x$ formation. Solomon et al. (1981) suggested the mechanism for this, which involves an H$_2$O ion cluster. Similar to the NO$_x$ effect discussed previously, the amount of total O$_3$ column loss depends on how easily HO$_x$ can propagate down into the mid-stratosphere, where O$_3$ is most abundant.

- H$_2$O is particularly sensitive to Lyman-$\alpha$ (121.6 nm) radiation, whereby it rapidly photolyzes to form HO$_x$. Chandra et al. (1997) suggested 30–40% and 1–2% change in terrestrial H$_2$O at 80 km and 60 km, respectively, in response to Lyman-$\alpha$ changes.

Absolute Lyman-$\alpha$ fluxes are especially large for A stars (and, to a lesser extent, F stars). They are about 30 times larger during the first 100 Myr after G-type stars have arrived at the zero-age main sequence (Ribas et al., 2005), so their exoplanets are the most likely candidates to lose their atmospheric H$_2$O via this mechanism, assuming a low-opacity atmosphere.

Ozone and dynamics: Terrestrial exoplanets with stronger differential heating gradients compared to those of Earth will feature a stronger equator-to-pole circulation.
On Earth, for example, slowing this circulation would imply a change in the amount of O$_3$ found in the tropics (where it is formed) relative to the amount of O$_3$ at higher latitudes, to where it is transported. Other effects like strong temperature gradients would potentially influence such effects (Spiegel et al., 2009).

Orographic features (mountains) also play an important role. On Earth, the Northern Hemisphere is much more mountainous than the Southern Hemisphere. Surface airflow over mountains leads to waves being excited, which carry heat and momentum up into the stratosphere and stimulate the equator-to-pole circulation, with the result that the Northern Hemisphere winter stratosphere is typically 10–20 K warmer than the Southern Hemisphere winter stratosphere (WMO, 1998). There is, however, no data for this effect over Earth’s history, so the effect is difficult to quantify for different topologies. On a cloud-free planet with surface features like those of Earth, the diurnal flux variation in the visible caused by different surface features rotating in and out of view could be high, assuming hemispheric inhomogeneity (Ford et al., 2001; Seager and Ford, 2002). When the planet is only partially illuminated, compared to a fully illuminated case, a more concentrated signal from surface features could be detected as they rotate in and out of view.

Methane (CH$_4$): Methanogen sources have quite specific temperature (and UV) dependencies that vary with species and environment (e.g., soil type) (Nozhevnikova et al., 2003). On early Earth, atmospheric sinks and geological sources may have been much stronger than they are today (Kasting and Catling, 2003); therefore,

- terrestrial exoplanets with fast tectonic activity and low O$_2$ may favor higher CH$_4$ while
- terrestrial exoplanets with some O$_2$ may favor fast CH$_4$ removal via OH.

Nitrous oxide (N$_2$O): N$_2$O is formed via denitrification in soil, which, like methanogenesis, is dependent on the temperature and the soil type (Li et al., 1992).

- N$_2$O is destroyed mainly via UV radiation, which suggests that strong UV fluxes could lead to strong photolytic N$_2$O loss.

It is probably not useful to apply derived physical N$_2$O relationships to exoplanet conditions since responses (e.g., of denitrifying bacteria) can be species specific and finely tuned to Earth conditions.

Biomarker molecules in Earth’s atmosphere respond to complex feedbacks, which sometimes produce widely differing results, for example, in chemistry-climate model responses (IPCC, 2001). Nevertheless, it can be assumed that the main influences are sufficiently well known to justify a discussion of biomarkers on Earth-like exoplanets [see Kaltenegger et al., 2010a (this volume)].

- O$_3$ is clearly sensitive to UV radiation in that it is both formed and destroyed in different regions of UV radiation, which depends on the radiative transfer in the atmosphere.
- Furthermore, O$_3$ concentrations are inversely proportional to temperature due to an increase in the sink: O + O$_3$ → 2O$_2$. This will be especially important for terrestrial exoplanets near the inner HZ or with strong greenhouse warming.
- O$_3$ is destroyed catalytically by HO$_x$, ClO$_x$, and NO$_x$—the latter may be particularly important for terrestrial exoplanets orbiting the HZ of M and some K dwarfs.

Ultimately, more-sensitive computer simulations that use atmospheric models are required to separate out the influences of the various feedbacks. H$_2$O, CH$_4$, and N$_2$O present additional measurement difficulties since they mainly exist in the troposphere below the cloud base.

- Warming the troposphere leads to more H$_2$O overcoming the cold trap at the tropopause and hence reaching the stratosphere. If this process proceeds too quickly, it will lead to removal of the O$_3$ layer via HOx destruction.

Estimating changes in CH$_4$ and N$_2$O sources on terrestrial exoplanets is difficult since, on Earth, they vary from organism to organism and are adapted to their particular biological niche.

- Regarding H$_2$O, CH$_4$, and N$_2$O sinks, enhanced stellar fluxes are expected to lead to a faster direct photolytic sink, as well as faster removal via (CH$_4$ + OH) and (N$_2$O + O$_{1D}$), since the radicals OH and O$_{1D}$ are formed photolytically.

Regarding seasonal and diurnal chemical cycles, these are most easily detected for O$_3$ (again, because other biomarkers occur mainly in the troposphere, where photolysis rates are low). On Earth, O$_3$ column seasonal variations are in the region of about 20% for the natural cycle at midlatitudes and about 50% for human-induced O$_3$-hole variations poleward of about 60°.

- Clearly, in the case of terrestrial exoplanets, the strength of the biomarker seasonal signal will depend on the viewing geometry. Note that first-generation space missions will observe disk-integrated spectra of exoplanets with no spatial resolution.

If we view only one hemisphere, then the seasonal signal will be strong compared to instances where both hemispheres are viewed simultaneously. On Earth, a small seasonal O$_3$ signal still persists, even if we average data over both hemispheres. Austin (2002) suggested a 3% cycle in mean observed column O$_3$ (averaged from 65 S to 65 N, i.e., excluding the effects of the man-made O$_3$ hole), with peak values in the Northern Hemisphere spring (which does not translate into a feature that is remotely detectable). This result is related to hemispheric asymmetry—the meridional circulation is stronger in the north due to more wave stimulation from mountain ranges.

However, it is entirely feasible that seasonal and daily biomarker amplitudes for many terrestrial exoplanets could be greater than those of Earth. Larger obliquity, for example, leads to stronger seasonal variations in stellar flux and temperature. Increases in ellipticity lead to seasons of unequal duration, as on Mars, and larger differences between closest and farthest approach also lead to large amplitudes in seasonal fluxes and temperatures.
Bertrand et al. (2002) and Williams and Pollard (2003) performed sensitivity runs for an Earth-like exoplanet with changed orbital parameters (e.g., increasing ellipticity), using a climate model. The latter study suggested an intensely strong seasonality, for example, equatorial surface temperatures varying from zero in winter up to 80°C in summer that would potentially be a much stronger influence on chemical variation.

4. Conclusions

Studying biomarkers helps us understand the potential chemistry on exoplanets, different chemical cycles, as well as observed spectra. It is worth exploring the parameter space of biomarkers because we see only a very limited range here on Earth.

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Abbreviations

HZ, habitable zone; PAL, present atmospheric level.

References


