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Abstract. Considering the future importance of the search for evidence of primitive life on a distant planet, we have revisited some points of the O_2 and O_3 detection criteria.

The budget of free oxygen and organic carbon on Earth is studied. If one includes the organic carbon in sediments, it confirms that O_2 is a very reactive gas whose massive presence in a telluric planet atmosphere implies continuous production. Its detection would be a strong indication for photosynthetic activity, provided the planet is not in a runaway greenhouse phase.

In principle, the direct detection of O_2 could be possible in the visible flux of the planet at 760 nm (oxygen *A*-band) but it would be extremely difficult, considering the much larger flux from the star. The alternative *search for the 9.7* μm *absorption of* O_3 may be easier as the contrast with the star is improved by three orders of magnitude. An atmospheric model confirms that the O_3 column density is not a linear tracer of the atmospheric O_2 content as was found in the pioneer work by Paetzold (1962). However, the detection of a substantial O_3 absorption ($\tau > 25\%$) would indicate, within the validity of this model, a O_2 ground pressure larger than 10 mbar. The question is raised of whether this pressure is sufficient to indicate a photosynthetic origin of the oxygen. If the answer was positive, it would be an even *more sensitive test of photosynthetic activity than the detection of the oxygen A-band.* Further studies of these points are clearly needed before determining an observing strategy.

Key words: planetary systems – exobiology – origin of life – extra-solar planet – exo planet – life in the universe

1. Introduction

The search for evidence of primitive life on extraterrestrial planets will probably be of increasing importance in the future. Specially if the development of the SETI program does not give indications of technological signals, an important issue will be to decide where is the bottle neck: from plantery habitable conditions to actual appearance of primitive life or from primitive life to evolved and technological life?

Although we should be prepared to search for life quite different from that which we have on Earth, Owen (1980) has argued that, if based on chemistry, alien life is likely to rely on carbon chemistry and liquid water. Silicon chemistry and liquid ammonia, for instance, seem less favorable.

Looking for life implying photosynthesis may be not too restricted an approach. The first idea is to search for the signature of chlorophyll-like molecules. However, we do not know where such a signature should be and, more important, this signature could be quite weak. In the case of the Earth, the absorption of the visible light reflected by the planet is only about 2% at the maximum of the chlorophyll absorption bands (420 and 660 nm).

Considering the situation in the Solar System, Lovelock (1975) concluded that the coexistence of gases in a mixture which is out of thermodynamical equilibrium (e.g. O_2 and CH_4) is a strong, although not certain, indication of biological activity.

Owen (1980) considers that the massive presence of O_2 in the atmosphere of a telluric planet with its reducing rocks (ferrous oxides) is indicative of photosynthesis activity but for the short period of a possible "runaway greenhouse" phase when the photolysis of H_2O can be a major, but time-limited, source of oxygen. Otherwise, in a cool atmosphere, water is protected from getting into its upper parts where it can be photolysed by a cold trap that makes it fall down as snow or rain. Then, the massive presence of O_2 in an atmosphere (0.1–0.2 bar) and a moderate temperature (300 ± 50 K) would be a strong indication of photosynthesis based life in a distant planet.

In this paper, we want to study the budget of the different oxygen and carbon reservoirs on Earth to check whether they are compatible with a biological origin of the

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atmospheric oxygen. We also discuss the relevance of detecting O_3 in the IR (9.7 μm) as a tracer of O_2 into the atmosphere.

2. Budget of free oxygen and organic carbon on Earth

The global reaction of photosynthesis can be written as:

$$CO_2 + H_2O + 2h\nu \rightarrow (CH_2O) + O_2. \quad (1)$$

(CH_2O) is symbolic for a typical organic molecule such as a glucide – $(CH_2O)n$ – the organic carbon involved in such species is partially reduced and can be easily distinguished from oxidized carbon in CO_2 or carbonates. The reduced O_2 goes into the atmosphere and may oxidize rocks or organic carbon.

If atmospheric O_2 on Earth has a photosynthetic origin and organic C does not have another sink than oxidation by oxygen, there must be more, or as much, C atoms in a reduced form than O_2 molecules in the atmosphere. This is not obvious if one considers the respective amounts of species in the atmosphere and in the biomass and it warrants a more detailed study.

The different reservoirs of O_2 and C can be measured by mass or equivalently by their thickness if spread in a uniform layer covering the whole Earth surface, with an arbitrary specific mass of 1 g cm^{-3}. One has the relation:

$$1\,\text{m} \leftrightarrow 5.15\ 10^{20}\,\text{g}.$$

This way of measuring the reservoirs is rather pictorial. For instance, we can readily appreciate the amount of atmospheric O_2 or living biomass on lands.

Table 1 shows the contents of the different reservoirs of free oxygen and organic carbon as reported by Siegenthaler (1986). As expected, the oxygen amount (2.3 m) is much larger than the carbon one contained in the biomass (6 mm) or in fossil fuels (11 mm). But *the key reservoir of reduced carbon is organics in sediments* (23 m). Sediments contain a substantial fraction of organic carbon (mostly in clays and shales where it represents ~1% of the mass) besides the inorganic one (carbonates). As a result, the total reservoir of organic carbon is significantly larger than that of free oxygen and this is *compatible with a photosynthetic origin of atmospheric* O_2. This is in agreement with the conclusions of past works (e.g. Walker 1977).

Table 1. Major reservoirs of free O_2 and organic carbon (adapted from Siegenthaler 1986). The amounts are expressed in thickness of a hypothetical layer of the species spread on the Earth surface that would have a specific mass of 1 g cm^{-3}. The equivalence with the reservoir mass is: 1 m↔5.15 10^{20} g. [(−3) means 10^{-3}]

Reservoir	h (m)
1) O_2 in atmosphere	2.3
dissolved in oceanic water[a]	<8(−3)
2) Organic carbon	
–Biomass --land (living)	1.1(−3)
--land (humus)	3(−3)
--ocean (living)	6(−6)
--ocean (dissolved)	2(−3)
–Fossil fuels	1.1(−2)
–Sediments: organic C	23
(inorganic C)	(120)

[a] Based on less than 5 ml of O_2 STP dissolved per litre of water when averaged over the ocean depth.

Reaction (1) implies that each time an organic carbon atom has been produced by photosynthesis in the past, an oxygen molecule has been released. The production of 23 m of reduced C has released 61 m of free O_2. It is 26 times the present amount of atmospheric oxygen (2.3 m). Then, most of the photosynthetic oxygen produced during geological time has been removed again and fixed in rocks by oxidation of sulfur and iron compounds. Oxygen has been in the Earth's atmosphere at the present level for the last $\tau_1 = 5\ 10^8$ yr (Holland 1984). It means that the production flux times τ_1 has given a O_2 amount of 61 m. On the other hand, the removing flux would make O_2 vanish, if production stops, in the residence time τ_r. Equaling both fluxes leads to: $\tau_r = \tau_1 \times 2.3\,\text{m}/61\,\text{m}$, or a residence time $\tau_r = 2\ 10^7$ yr, in good agreement with oceanographic estimates (Broecker & Teng 1982). This residence time is short, so a continuous production of oxygen appears to be necessary to maintain a substantial fraction of this gas in an atmosphere. This strengthens the argument by Owen (1980) that the *massive presence of* O_2 *in the atmosphere of a planet* which is not in a runaway greenhouse phase due to water *is a strong indication of photosynthetic activity.*

The mere study of the IR emission by the planet could be insufficient to exclude that it is in a runaway greenhouse phase, because it may come from the cold upper parts of its atmosphere (e.g. Venus) but, anyway, this phase is of short duration and the detection of O_2 in several planets would be statistically meaningful.

3. Is O_3 a good tracer of atmospheric O_2?

3.1. How to detect O_2?

Owen (1980) has suggested to detect the presence of O_2 in a distant atmosphere by looking for its A-band absorption at 760 nm. However, this is a very difficult observation. Apart from the favorable case of a planet eclipsing a star (Schneider 1992), one has to image the star and the planet, block the star light and make a spectrum of the planet light. The star to planet flux ratio is $5\ 10^9$ in the case of Sun/Earth. This indicates how difficult such an observation would be.

3.2. An interesting alternative: the detection of ozone

In 1986, Angel pointed out that this ratio decreases by almost three orders of magnitude if fluxes are considered

in the IR, around 10 μm. In this spectral range, he noticed that Earth is the only telluric planet that exhibits a strong O_3 absorption line ($\lambda = 9.7$ μm, $\tau \sim 0.6$). The formation of O_3 in the Earth atmosphere requires O_2 molecules and if O_3 can be considered as a good tracer of the presence of O_2 in an atmosphere, its detection could be easier. In fact, Angel proposed a telescope (16 m diameter in space, passively cooled to 80 K) which could be built in the near future but for financial constraints and could make such an observation.

The point we want to examine here is the quality of O_3 as a O_2 tracer. It is clear that such a costly project can be considered only if we think that it has a safe basis.

One can readily think of an objection. In the Earth's atmosphere, O_3 is formed in the upper layers, down to an altitude such that the optical depth of the oxygen column density above it is a few unities in the UV spectral range that dissociate O_2 into atomic O. As oxygen is abundant on Earth, this altitude is high (~ 20 km) but if oxygen was less abundant, one can imagine to form a similar quantity of O_3 but lowering its location, so that the oxygen column above it would be still sufficient. In fact, the ratio of ozone to oxygen column densities is 200 times larger on Mars than on Earth (Traub et al. 1979).

Ozone seems to be a non-linear tracer of the amount of oxygen in an atmosphere so it requires a more quantitative study.

3.3. A model for O_3 column density as a function of O_2 amount in an atmosphere

A one-dimensional model which computes the total column of ozone as a function of the partial pressure of O_2 at ground is used. For a first study, we assume an atmosphere which has several similarities with the Earth's. The incoming UV radiation is that of the Sun on the Earth. The deposition velocity of ozone at ground is assumed to be 0.075 cm s^{-1} which corresponds to the deposition velocity on water or snow (Muller 1992). The temperature vertical profile is the same as the one for Earth.

The atmosphere is assumed to contain oxygen and its derivatives as active gases and inactive species such as N_2 on the Earth. The relative abundances of the two categories can be varied. The photochemical production and destruction of ozone are then only governed by the Chapman cycle (Chapman 1930):

$$O_2 + h\nu \xrightarrow{J_1} O + O, \quad (1)$$

$$O + O_2 + M \xrightarrow{k_1} O_3 + M, \quad (2)$$

$$O_3 + h\nu \xrightarrow{J_2} O_2 + O, \quad (3)$$

$$O + O_3 \xrightarrow{k_2} 2O_2, \quad (4)$$

$$O + O + M \xrightarrow{k_3} O_2 + M, \quad (5)$$

where

— M is any molecule, mostly O_2 and N_2 on Earth,

— J_1 and J_2 are, respectively, the photo-dissociation coefficient of molecular oxygen and ozone, which depend on the UV flux at the altitude z. This flux is decreasing as the altitude decrease due to its absorption by O_2 ($\lambda < 242$ nm), O_3 (mainly $\lambda < 320$ nm) and Rayleigh scattering;

— k_1, k_2 and k_3 are, respectively, the rate coefficients of reactions (2), (4) and (5) which depend on temperature T

$$k_1 = 6\,10^{-34}(T/300)^{-2/3},$$

$$k_2 = 8\,10^{-12}\exp(-2060/T),$$

$$k_3 = 5.2\,10^{-35}\exp(900/T).$$

Although reaction (3) is very fast ($J_2 = 10^{-2}\,s^{-1}$ at the top of the Earth atmosphere), the photo-dissociation of ozone by this reaction is not a net loss for this molecule. Indeed, the atomic oxygen produced in this reaction easily reproduces ozone by the equally fast reaction (2). Assuming the photochemical equilibrium for O_3 and neglecting reaction (4) leads to a relation between the concentration of O and O_3 which can be written as

$$\frac{[O]}{[O_3]} = \frac{J_2}{k_1[O_2][M]}. \quad (6)$$

The net loss of ozone is in fact the loss of odd-oxygen $O_x = O + O_3$ by the much slower reactions (4) and (5).

Vertical distribution of ozone is not only governed by photochemical reactions but also by transport processes. In a one-dimensional model, the vertical transport is represented by an effective vertical eddy diffusion coefficient K. On the Earth, the vertical profile of this coefficient is computed to fit the model results with the observations. This profile has been assumed in the calculations.

At each altitude z between 0 and 60 km, by step of 1 km, the evolution of the odd-oxygen concentrations is given by the following equation:

$$\frac{\partial[O_x]}{\partial t} = 2J_1[O_2] - 2k_2[O][O_3] - 2k_3[O][O][M] - \frac{\partial \Phi}{\partial z}, \quad (7)$$

where

$$\Phi = -K[M]\frac{\partial}{\partial z}\left(\frac{[O_x]}{[M]}\right) \quad (8)$$

and taking into account (6)

$$[O] = \frac{R[O_x]}{(1+R)}, \quad (9)$$

$$[O_3] = \frac{[O_x]}{(1+R)}, \quad (10)$$

where

$$R = \frac{J_2}{k_1[O_2][M]}.$$

J_1 and J_2 are averaged values on a diurnal cycle computed in equinox conditions at 30 N on the Earth. They depend on the O_3 concentrations at each altitude z. In consequence, the system of Eqs. (7) is solved by iterations. The computed O_3 vertical concentration profile is used to compute J_1 and J_2 for the next iteration, until convergence is obtained. Once O_x vertical profile is computed, O_3 vertical profile is obtained using (10). The integration of the O_3 concentration from 0 to 60 km gives the ozone total column. Figure 1 shows the ozone total column as a function of the O_2 partial pressure at ground, assuming a total pressure at ground of 10^5 Pa (1 bar or 1 Earth atmosphere). Also shown is the ozone total column of the Earth.

Our results are in good agreement with the previous work by Paetzold (1962) for $p_{O_2}=10^{-3}$ to 1 bar. The model reproduces the Earth case only within a factor 1.4 because destruction of ozone by catalytical cycles involving hydrogen, nitrogen and chlorine species are not taken into account.

The model also reproduces the case of Mars within a factor of 2. This point gives some confidence in the model generality and capability to describe the O_3 amount in an atmosphere which is not strictly Earth like. Specifically, the O_2 amount seems to be a more crucial parameter to determine the O_3 column density than the total gas pressure or the star flux.

The model results are dependent on the temperature and pressure profiles of the planet. Indeed, rate constants are temperature dependent and changes in the total concentration change the oxygen/ozone ratio [relation (6)]. Other calculations have been made *changing the temperature profile* in the following manner: the maximum of temperature is located at the maximum of heating of the atmosphere due to the absorption of UV by ozone as in the case of the Earth; this maximum of temperature has been assumed to be the same as in the Earth; the results indicate *maximum differences of 30% in the worse cases*, which is negligible for our purpose.

Second, the *total pressure* at ground (and therefore the vertical pressure profile if the gravitational force is the same) has been changed. Figure 2 shows the results for a total pressure at ground of 0.1, 1 and 10 bar. We remark that the corresponding change in O_3 total column is less than a factor 2 for partial pressure of O_2 ranging from 10^{-3} to 10^{-1} bar.

These tests indicate that the relationship between the O_3 column and O_2 partial pressure of an atmosphere shown in Fig. 1 is rather stable with respect to different variations of the atmosphere parameters.*

3.4. *Implications of the model results*

Clearly, O_3 is a non-linear tracer of the O_2 amount of an atmosphere. For instance, when the O_2 ground pressure varies from 10^{-2} to 1 bar, the O_3 amount varies only by a factor of 3.

However, it does not mean that the detection of O_3 in an extrasolar planet atmosphere would not be a good criterion for exobiology. To be detectable in such difficult conditions, the 9.7 μm absorption of O_3 would have to be rather strong, say larger than half that of the Earth $(I/I_0)_{\text{Earth}} \sim 50\%$). If we assume that the optical depth is proportional to the O_3 column density,** according to our model, it implies that the *oxygen pressure in such atmosphere would be larger than 10 mbar.* If the greenhouse runaway phase can be eliminated, would such a pressure be sufficient to indicate a continuous photosynthetic production of O_2? We think that this is an *open question* that

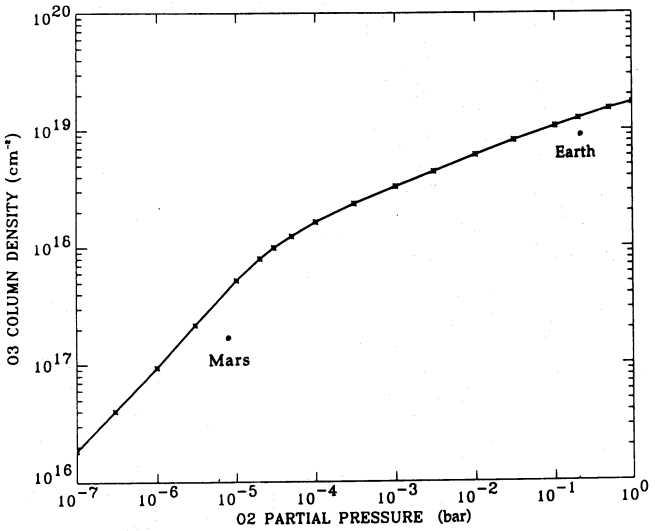

Fig. 1. Column density of ozone as a function of the ground pressure of oxygen as resulting from the atmospheric model. It reproduces the case of Earth and Mars, within a factor of 1.4 and 2, respectively

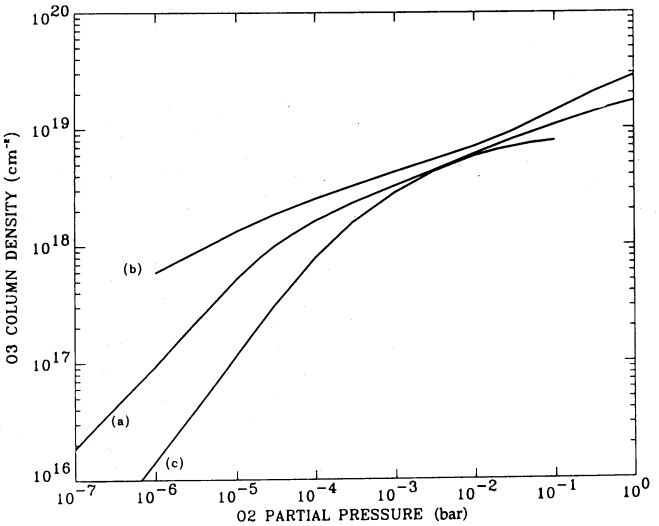

Fig. 2. Same as Fig. 1, but with different total atmospheric pressures: (*a*) $P_{\text{tot}}=1$ bar; (*b*) $P_{\text{tot}}=10$ bar; (*c*) $P_{\text{tot}}=0.1$ bar

should be worked out in the future, considering its implications. If we refer to the past of Earth, the answer would probably be positive (Holland 1990). In that case, *the detection of the* 9.7 μm *band of* O_3 *would be an even more sensitive test for the presence of* O_2 *than the search for the oxygen A-band in the visible.* As a matter of fact, with $p_{O_2} = 10$ mbar, the latter would be quite weak, with an optical depth of $7\,10^{-3}$ when measured with resolution $R = 40$ (Owen 1980) and would not be detectable.

An interesting way to check whether $p_{O_2} = 10$ mbar could have an abiotic origin is to consider the case of a model of Mars' atmosphere. On this planet, O_2 is presently 0.13% of the atmosphere. Would the percentage change if the surface pressure on Mars were increased 150 times and the temperature increased as well as due to the CO_2 greenhouse effect? Could one reach 10 mbar of O_2 for a 1 bar Martian atmosphere? This question needs a good planetary atmosphere model to be answered. We are considering the possibility of developing such a model in collaboration with planetary science colleagues.

4. Conclusion

The budget of free oxygen and organic carbon on Earth confirms that O_2 is a very reactive gas whose massive presence in a telluric planet atmosphere implies a continuous production. Its detection would be a good indication for a strong photosynthetic activity, provided the planet is not in a runaway greenhouse phase due to H_2O. It should be noted that the reverse is not true. A photosynthetic activity is possible on a planet that has not yet succeeded to oxidize a strongly reducing crust. The resulting low concentration of O_2 in the atmosphere would not be a proof of the absence of life on this planet. This was the case for the Earth from -3.5 to -0.5 Gyr. In addition, exotic forms of life may exist that would not be detected by the search for O_2.

In principle, the direct detection of O_2 could be possible in the visible flux of the planet at 760 nm (oxygen A-band) but it would be extremely difficult, considering the much larger flux from the star. The alternative search for the 9.7 μm absorption of O_3 may be easier as the contrast with the star is improved by three orders of magnitude. A simple atmospheric model indicates that the O_3 column density is not a linear tracer of the atmospheric O_2 content. However, the detection of a substantial O_3 absorption ($\tau > 25\%$) would indicate, within the validity of this model, a O_2 ground pressure larger than 10 mbar. The question is raised of whether this pressure is sufficient to indicate a photosynthetic origin of the oxygen. If the answer was positive, it would be an even *more sensitive test* of photosynthetic activity than the detection of the oxygen *A*-band. Further studies of these points are clearly needed before determining an observation strategy.

Note that the spectra of both Jupiter and Saturn show dips at 9–11 μm due to NH_3 and PH_3 that could be confused with the signature of O_3. But the conditions for these gas to be present in a planetary atmosphere are specific enough to prevent any confusion between the identification of O_3 and that of NH_3 or PH_3.

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Notes added in proof

* The incidence of the spectral composition of the stellar flux irradiating the planet will be studied in the near future.
** The assumption that the O_3 band optical depth is proportional to the O_3 column density is crude, so we plan to make a precise calculation of the dependence of the 9.7 μm band optical depth upon the ground O_2 pressure of the planet.