

# Is the presence of H<sub>2</sub>O and O<sub>3</sub> in an exoplanet a reliable signature of a biological activity?

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**Abstract.** We revisit the validity of the presence of H<sub>2</sub>O and O<sub>3</sub> in the atmosphere of an extra-solar planet as a criterion for the presence of biological activity in progress. We consider different objections to the criterion and specify the conditions for it to apply.

Noll et al. (1997) have recently suggested a new process: the synthesis of O<sub>2</sub> by particle bombardment of pre-cometary icy grains in the protoplanetary nebula, subsequent input of the species into the planet's atmosphere by comet impacts and UV synthesis of O<sub>3</sub>.

We estimate the amount of O<sub>2</sub> produced by this process in comets within the framework of recent disk models and find:  $[O_2]/[H_2O] < 1.3 \cdot 10^{-7}$ , a value significantly less than that suggested by Noll et al. Our result is in agreement with the *absence* of O<sub>2</sub> detection in Halley's comet by the Giotto HIS mass spectrometer (upper limit:  $[O_2]/[H_2O] < 0.5\%$ ).

Further, the geological record from the Young Earth shows that the heavy cometary bombardment prevailing at that time had *not* been able to build a O<sub>2</sub> rich atmosphere on our planet.

We conclude that Noll et al.'s objection fails. The presence of abundant H<sub>2</sub>O and O<sub>3</sub> does demonstrate the presence of biological activity on an extra-solar planet located in the Continuously Habitable Zone of its star (0.95-1.15 AU for a Sun-like star).

**Key words:** comets: individual: Halley – comets: general – solar system: formation – planetary systems

## 1. A new field opens in astronomy

In 1995, a new chapter of astronomy opened when Mayor and Queloz reported the discovery of a Jovian extra-solar planet (exoplanet) around the main sequence star 51 Peg. This discovery, rapidly followed by others (Butler & Marcy, 1996), was not that of the first exoplanet. Wolszczan (1991) had already unambiguously identified planets around the pulsar PSR 1257+12, but the observation of 51 Peg opened the field of observational Bioastronomy out of the Solar System.

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The next steps in this quest for extra solar life are the search for exoplanets that are:

- (i) telluric,
- (ii) habitable,
- (iii) inhabited by micro-organisms.

Strategies for items (i) to (iii), aiming at obtaining "yes or no" answers at each step have already been proposed. In this paper, we concentrate on item (iii).

Owen (1980) showed that exo-biological activity is most likely based on carbon chemistry with H<sub>2</sub>O as a solvent (see also Léger, 1997). He showed that if biological activity on a telluric planet develops on a large scale, it necessarily produces a large quantity of O<sub>2</sub>. As this gas is very reactive with reducing rocks and gases emitted by volcanoes, it would disappear in a short time in the absence of a continuous production (4 Myrs on Earth; Kasting, personal comm.; Holland, 1978). So he concluded that the abundant presence of O<sub>2</sub> in the atmosphere of an exoplanet demonstrates the presence of life.

Another step was made when Angel et al. (1986) showed that O<sub>3</sub>, whose detection is easier, is a tracer of O<sub>2</sub>. The spectral signature of ozone occurs in the IR (9.6 μm) whereas that of molecular oxygen is in the visible (e.g. 760 nm). For a solar-type star, the ratio of planet to star luminosities improves by almost 3 orders of magnitude when one moves from the visible to the mid-IR (Bracewell, 1978).

IR interferometric missions in Space have been proposed to search for telluric exoplanets around nearby stars and perform a spectroscopic analysis of their atmosphere in the mid-IR, searching for the signatures of CO<sub>2</sub> (15 μm), H<sub>2</sub>O (6-8 μm), O<sub>3</sub> (9.6 μm) and CH<sub>4</sub> (7.7 μm) (DARWIN, Léger et al., 1993a, 1996; OASES, Angel & Woolf, 1997; TPF, Beichman, 1996).

If the preceding statements are correct, such missions should be able to answer questions (i) to (iii). However, Noll et al. (1997) have recently claimed that the detection of O<sub>3</sub> is not an unambiguous identification of Earth-like biology because abiotic processes may cause O<sub>3</sub> to be present.

Considering the major scientific significance of this topic, and the high cost of the missions required to perform the search,

careful study of the validity of this objection is needed. This is the goal of the present paper.

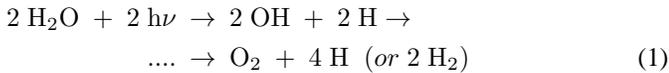
## 2. The H<sub>2</sub>O - O<sub>3</sub> criterion

It is important to specify the conditions when the simultaneous detections of H<sub>2</sub>O and O<sub>3</sub> becomes a proper test for the presence of a biological activity on an exoplanet. The main concern is, of course, to avoid false positives i.e. detection of *abiotic* O<sub>3</sub>.

### 2.1. Possible sources of abiotic O<sub>2</sub>

In his original paper, Owen (1980) already considered this question and since that time, it has been revisited several times. Before Noll et al.'s paper, the main process considered for producing large amounts of abiotic O<sub>2</sub>, and consequently O<sub>3</sub>, was the photodissociation of gases as CO<sub>2</sub> and H<sub>2</sub>O. The former can produce only very limited quantities of O<sub>2</sub> (Rosenquist & Chassefière, 1995) but the latter requires a more detailed study.

The corresponding chain of reactions can be summarised as:



If hydrogen escapes from the atmosphere of the planet, the result is the presence of abiotic O<sub>2</sub> (Chassefière, 1996) that in turn can produce O<sub>3</sub> through additional photochemical processes.

### 2.2. Telluric planets with temperate climates

When a planet has a surface temperature similar to that of the Earth, a cold trap develops in its atmosphere that precipitates most of the evaporated H<sub>2</sub>O as rain or snow and prevents it from becoming a major constituent of the upper layers of the atmosphere where liberated hydrogen could escape. The hydrogen produced by H<sub>2</sub>O photolysis has then to go through a long diffusive path before escape becomes possible. During this journey there is a high probability of recombining with oxygen and rebuilding H<sub>2</sub>O. The overall destruction rate of H<sub>2</sub>O and production of abiotic O<sub>2</sub> is then very low. On Earth, this production is only 10<sup>-6</sup> times that by biological photosynthesis (Walker 1977) i.e. 1 ppm is abiotic.

Is a cold trap expected on a telluric exoplanet? For planets with plate tectonics which are located inside the Continuously Habitable Zone (CHZ) of their star (Kasting et al. 1993a), the CO<sub>2</sub> cycle provides an efficient regulation of the surface temperature and provides the conditions for the development of this cold trap. An increase of the temperature produces an increased of H<sub>2</sub>O evaporation, more rain, which in turn dissolves more atmospheric CO<sub>2</sub>. The acidic water attacks silicate rocks and fixes the CO<sub>2</sub> in the planet's mantle as carbonate sediments. The greenhouse heat trapping due to CO<sub>2</sub> decreases and the surface temperature cools back (Kasting 1997; Duplessy &

Morel 1990). Conversely, a surface cooling decreases the water evaporation and decreases the fixing rate. As plate tectonics and volcanism provide a steady source of CO<sub>2</sub>, the concentration of this gas increases in the atmosphere and the resulting greenhouse effect combats the initial temperature decrease.

This regulation has to be very efficient because it has never failed during the 4.6 Gyrs of the Earth's life, although plate tectonics has produced major changes in the distribution of continents and oceans (e.g. opening and closing the Straits of Gibraltar) that changed Earth's albedo and might have caused a climatic runaway.

### 2.3. Greenhouse runaway

The CO<sub>2</sub> regulation is efficient as long as the planet temperature is not high enough to prevent the formation and preservation of carbonates. Conservatively, Kasting et al. (1993a) estimated that planets at normalised distances from their star larger than 0.95 AU do have a cold trap. The normalisation is a multiplication of the actual distance by  $(L/L_{\odot})^{1/2}$  where  $L$  and  $L_{\odot}$  are the star and Sun luminosities. Normalization results in black sphere planet temperatures that are independent of the star luminosity.

If the planet is too close to its star, the regulation by CO<sub>2</sub> can fail and the planet suffers a runaway greenhouse effect. This probably happened to Venus. When the trap is not cold enough, large quantities of H<sub>2</sub>O vapor enter the upper atmosphere, the water vapor greenhouse effect increases, as does the surface temperature. More water evaporates, increasing the heating and so on. Water becomes a major constituent of the atmosphere and its UV photolysis takes place in the highest layers of the atmosphere. Hydrogen can escape after a short diffusion path during which the probability of rebuilding a water molecule is small. Massive hydrogen escape and *abiotic* O<sub>2</sub> production result.

However, there are several criteria to recognise such a situation:

(1) the temperature runaway is expected only for planets at renormalised distance from their star significantly smaller than 0.95 AU. In the missions proposed to search for life by using the presence of O<sub>3</sub> as a criterion, both the star luminosity and planet separation from it will be directly observable, and it will be possible to determine the black sphere temperature independent of the star's distance. This will enable us to estimate whether a planet can be in a hot and moist runaway phase.

(2) a runaway process is a fast event. The time required for photodissociating the whole content of free H<sub>2</sub>O at the surface of the planet is relatively short (0.1- 0.3 Gyr). The duration of the following phase, when O<sub>2</sub> is being depleted from the atmosphere will depend upon the rate at which O<sub>2</sub> sinks can capture oxygen. It can last longer than the first phase because the O<sub>2</sub> sinks can be temporary saturated (finite volcanic outputs...). Consequently, if the criterion is: "the *simultaneous* presence of O<sub>2</sub> and H<sub>2</sub>O", the probability of finding an exoplanet in such a phase is small. If a sample of planetary systems can be studied, only a small fraction of them could be in such a situation (Owen, 1980), in

addition to the characteristic feature of their location out of the CHZ of their star.

In conclusion, this production of abiotic  $O_2$  will not be misinterpreted as evidence of photosynthesis.

#### 2.4. Icy planet without volcanism

There is another situation that can lead to an atmosphere rich in abiotic  $O_2$ : that where oxygen sinks are inactive which allows the low production of  $O_2$  by UV photolysis to accumulate (Kasting, 1997).

When a planet is small enough, its volcanism disappears some time after the planet formation and so do the associated oxygen sinks. Quantitative calculation should be done but there is probably room between the sizes of Earth and of Mars for a planet large enough to retain a thick atmosphere (0.1-10 bar) but small enough for volcanism to vanish after 2 Gyr or thereabouts.

The sink due to water weathering can also be lacking if the planet is cold enough to have very low water evaporation, scarce snow falls but no liquid water rainfall.

Consequently, a planet with a size in between those of Earth and Mars, located outside the CHZ, could have an atmosphere rich in abiotic  $O_2$ .

There are features that would allow *the identification of this situation* too:

- (i) the planet is located outside CHZ;
- (ii) it has a small size;
- (iii) the temperature of its surface is lower than the  $H_2O$  freezing point;
- (iv) the strength of the water bands in the planet spectrum are weaker because of the low water content of its atmosphere.

Modelling is needed to quantify points (ii) and (iv).

This production of abiotic  $O_2$  will not be misinterpreted as evidence of photosynthesis either.

#### 2.5. Formulation of the $H_2O - O_3$ criterion

The preceding considerations lead to the formulation:

”a simultaneous detection of significant amounts of  $H_2O$  and  $O_3$  in the atmosphere of an exoplanet located in the Continuously Habitable Zone of its star, i.e. at renormalised distances from the star between 0.95 and 1.15 AU, is a good signature of biological activity”.

We have shown that this criterion does not suffer from a confusion with abiotic production by UV photolysis in the planetary atmosphere. Now, we consider the objection by Noll et al. (1997) where abiotic presence of  $O_2$  is due to infall of comets whose icy grains would be rich in  $O_2$ .

### 3. Could cometary bombardment be at the origin of abiotic $O_3$ on a telluric planet?

#### 3.1. Noll et al.'s hypothesis

A tenuous  $O_2$  atmosphere has been found on Europa (Hall et al., 1995) and Ganymede that is attributed to the sputtering of

oxygen from  $H_2O$  ice by energetic particles. Noll et al. (1997) have found the UV spectral signature of  $O_3$  in the icy satellites of Saturn, Rhea and Dione. They have explained their observations as the result of particle bombardment of  $H_2O$  ice in the high radiation flux environment of Saturn's magnetosphere producing  $O_2$  and  $O_3$ . Then, these authors have stated that *if* pre-cometary grains have experienced a similar situation and contain  $O_3$  and  $O_2$  in their thin outer layers, comets would contain a significant fraction of these gases. As comets have probably brought some fraction of the water content of telluric planets (Owen et al., 1992), Noll et al. have concluded that this could be an important source of abiotic  $O_2$  and  $O_3$  which would falsify the preceding criterion for detecting photosynthetic activity.

The presence of abiotic  $O_3$  on icy planetary objects which are atmosphereless and located at (renormalised) distances larger than the icy frontier (4 AU) could not be confused with the  $O_3$  resulting from photosynthesis in a telluric planet atmosphere. The nature of objects will be clearly established: the distance of the planet to its star will be measured and the shape of the IR spectrum will indicate the temperature of the object, 100 K instead of 300 K. The real issue is the proposed input of  $O_2$  into telluric planet atmospheres by cometary impacts and subsequent  $O_3$  formation.

#### 3.2. The case of the young Earth

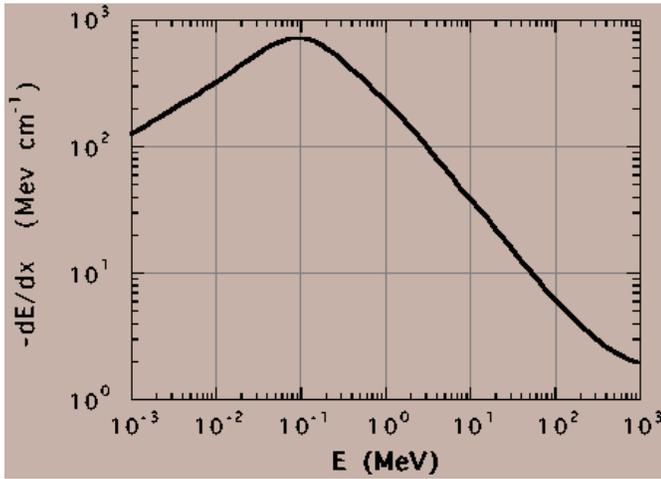
The geological record of Earth provides highly *significant evidence*. Despite any input of  $O_2$  by comets, early Earth did not build an  $O_2$  rich atmosphere. This was despite a cometary bombardment that was probably much higher near the origin of a telluric planet than later on. Banded iron formations are found in sediments older than 1.9 - 2.2 Gyrs ago (Ga), indicating the absence of a strongly oxidising atmosphere. Quantitatively, Kasting (1987) argued that they tell us that the partial pressure of  $O_2$  was lower than 6 mbar. Other estimates point to still lower values.

Another piece of evidence of the very low  $O_2$  content of atmosphere of the Young Earth, if any, is the mere fact that we are here and that life has started earlier than 3.6 Ga (presence of stromatolite fossils) and possibly earlier than 3.8 Ga ( $^{13}C/^{12}C$  indications). There was not a large amount of free  $O_2$  in the Earth's early atmosphere, for this would have prevented the spontaneous, reducing chemistry necessary for the origin of life.

Since 2.5 Ga, the  $O_2$  content has rapidly increased. It is likely associated with a decrease in the  $O_2$  fixation rate due to a decline of volcanic reducing outputs ( $H_2 + CO + SO_2$ ). This decline was a consequence of progressive oxidation of the upper mantle due to the subduction of  $H_2O$ , its dissociation followed by outgassing and escape of  $H_2$  (Kasting et al 1993b). By no means was it due to an increase of the cometary bombardment.

### 4. $O_2$ Production by particle irradiation in pre-cometary grains

Is there a major difference between the particle irradiation of the Saturn's icy satellites and that of pre-cometary grains? The



**Fig. 1.** Energy loss of protons in H<sub>2</sub>O ice ( $\rho = 0.9 \text{ g cm}^{-3}$ ) versus proton energy (from code SRIM-96 by Biersack & Ziegler, 1996)

former are in an environment where the particle flux is large because of Saturn's magnetosphere and the latter may be efficiently protected from the protostar's wind by the dense protoplanetary nebula. We are asking whether the premise by Noll et al. is correct: the integrated particle flux (fluence) received by pre-cometary grains in a protoplanetary nebula may not be sufficient to produce a significant amount of O<sub>2</sub> - O<sub>3</sub>. We will make a quantitative estimate of the oxygen production.

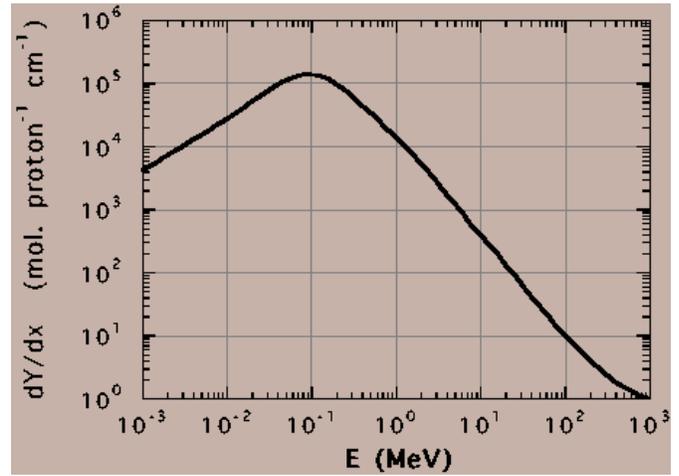
#### 4.1. Production of O<sub>2</sub> by proton irradiation of H<sub>2</sub>O ice

The chemistry induced by high energy particle irradiation of solids has been studied by different groups (e.g. Roessler, 1991). Specifically, the irradiation of H<sub>2</sub>O ice by protons leads to an erosion and production of O<sub>2</sub>. The former is attested by the decrease in the strength of the IR bands of H<sub>2</sub>O in an irradiated ice film and the latter by the outgassing of O<sub>2</sub> from the films (Rocard et al., 1986; Bénil, 1987; Bénil et al., 1987, 1991).

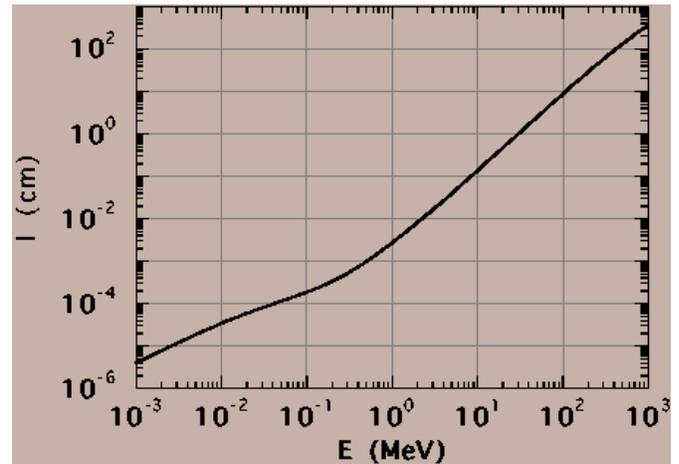
The yield of O<sub>2</sub> molecules per incident proton in ice, of prime importance for our purpose, is at most half the H<sub>2</sub>O molecule destruction rate,  $Y$ . Measurements of  $Y$  have been made by the authors named above. They have found that the yield per unit length,  $dY/dx$ , varies approximately as the square of the particle energy loss,  $(dE/dx)^2$ , and  $Y(30 \text{ keV}) = 3$  molecules/proton.

The energy loss of protons in H<sub>2</sub>O ice has been studied (Biersack & Ziegler, 1996) and is shown in Fig. 1. The corresponding function,  $dY/dx(E)$ , is shown in Fig. 2. The range (mean free path) of protons in ice and the integrated quantum yield,  $Y(E)$ , of ice erosion are shown in Figs. 3 and 4 respectively. It is remarkable that, for high energy cosmic rays, a large number of H<sub>2</sub>O molecules can be destroyed by a single proton, e.g. 120 molecules per 1 MeV proton. This phenomenon has been (incorrectly) called "giant sputtering" of ice.

If the proton irradiation of the grains in protoplanetary disks can be estimated, an upper limit of O<sub>2</sub> production in icy pre-cometary grains can be calculated and an upper limit of the [O<sub>2</sub>]/[H<sub>2</sub>O] mixing ratio in comets will result.



**Fig. 2.** Differential quantum yield of H<sub>2</sub>O erosion by protons in water ice, expressed in number of eroded molecules per proton per unit length, versus the proton energy. It is calculated by assuming its proportionality to the square of the proton energy loss per unit length in the material and scaled on experimental points (Rocard et al., 1986 ; Bénil, 1987 and Bénil et al., 1987, 1991)



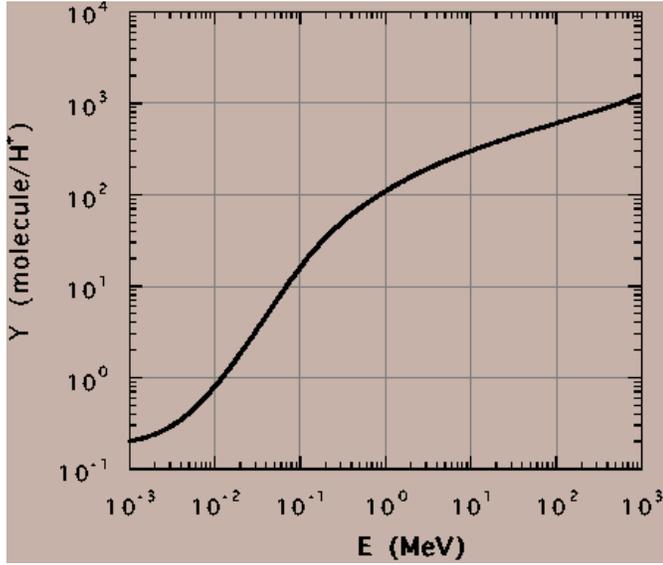
**Fig. 3.** Range or projected mean free path of protons in H<sub>2</sub>O ice ( $\rho = 0.9 \text{ g cm}^{-3}$ ) versus proton energy from code SRIM-96 by Biersack and Ziegler (1996)

#### 4.2. Expected proton flux in protoplanetary disks

Our present understanding of planetary and cometary formation in protoplanetary disks is based on the sedimentation and growth of dust grains, the formation of planetesimals, which are comets when located further out than the ice boundary, and their accretion into telluric planets or giant planet cores. During these processes, the major source of high energy particles is the protostar and its surroundings.

##### - Irradiation duration

The volume production of O<sub>2</sub> can be important only when the precometary grains are small because it occurs in their outer layers, at least for the moderate energy particles, the most abundant ones. Typical exposure time before growing to 1 cm is  $\Delta t = 10^5 \text{ yr}$  (Weidenschilling & Cuzzi, 1993).



**Fig. 4.** Quantum yield of H<sub>2</sub>O erosion by protons in a semi infinite water ice medium calculated with same assumptions as for Fig. 2. The large number of extracted H<sub>2</sub>O molecules per high energy proton is (incorrectly) called “giant sputtering”

#### - Disk structure

We use the standard “minimum mass” protoplanetary disk model (Beckwith et al., 1990; Cuzzi et al., 1993 ; Shu et al., 1997). In this model, the temperature  $T$ , surface density  $\sigma$ , disk thickness  $2h$ , and volume density  $\rho$  vary with reduced distance  $r = R/1$  AU to a Sun-like star as:

$$\begin{aligned} T(r) &= T(1) r^{-0.5}, T(1) = 280 \text{ K} \\ \sigma(r) &= \sigma(1) r^{-1.5}, \sigma(1) = 1700 \text{ g cm}^{-2} \\ h(r) &= h(1) r^{1.25}, h(1) = 4.1 \cdot 10^{-2} \text{ AU} \\ \rho(r) &= \rho(1) r^{-2.75}, \rho(1) = 1.4 \cdot 10^{-9} \text{ g cm}^{-3} \end{aligned} \quad (2)$$

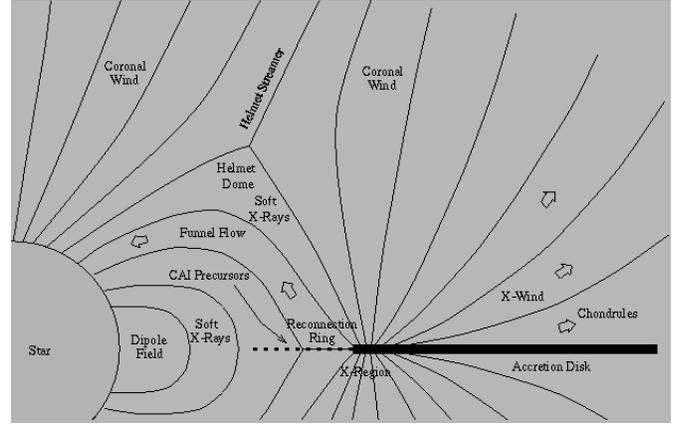
with cut off radii:  $r_{min} = 0.055$  ( $R_{min} = 12R_{\odot}$ ) and  $r_{max} \sim 100$ . The mass of the disk is  $M_{disk} = 2.3 \cdot 10^{-2} M_{\odot}$ .

Shu et al. (1997) have proposed a model for the production of high-energy particles by the star-disk system (Fig. 5). For our purpose, the crucial point is that there is *no major trajectory impinging on the disk* at distances where the pre-cometary grains are located ( $r > 4.3$  for  $T_{ice} = 135\text{K}$ ). This implies that the grains are not subject to particle irradiation because the direct irradiation in the disk plane is null. This model has been able to explain independent and unexpected observations in the Solar System, e.g. evidence of flash heating of the chondrules in chondritic meteorites and their containing short-life radioactive elements such as  $^{26}\text{Al}$  and  $^{53}\text{Mn}$ .

However, it cannot be excluded completely that, in special conditions, some magnetic field lines skim over the surface, with few of them penetrating into the disk. Below, we estimate an upper limit for O<sub>2</sub> synthesis by this hypothetical irradiation.

#### - High energy protons flux produced by protostars

The spectrum of protons emitted by protostars can be estimated



**Fig. 5.** Scheme of the model of a protostar and its disk by Shu et al. (1997). The matter flows follow the magnetic field lines. The inner part of the disk, the X-region, starts at  $12 R_{\odot} = 5.5 \cdot 10^{-2}$  AU for a solar mass protostar. Note that *no high energy particle impinges on the disk* (courtesy of Shu et al., 1997)

(Shu et al., 1997) using the X ray emission of these objects in dark clouds as observed by the satellite ASCA (Koyama et al., 1996),  $L_X = 3 \cdot 10^{30} \text{ erg s}^{-1}$  for 0.4 to 12 keV X rays, and the Sun as a model for the proton to X ray luminosity ratio,  $L_p(E > 10 \text{ MeV})/L_X = 3$  (Kahler, 1992 ; Haisch et al., 1995). Approximating the proton differential spectrum by that of the Sun (Van Hollebeke et al., 1975), we have:

$$dL_p/d\epsilon = 2 \cdot 10^{37} \epsilon^{-2.7} \text{ proton s}^{-1}, \quad \text{for } \epsilon > 10, \quad (3)$$

where  $\epsilon \equiv E/1 \text{ MeV}$

#### - Proton spectrum after shielding by the disk

This spectrum can be numerically computed from the energy loss curve (Fig. 1) and the initial spectrum  $\Phi_1(\epsilon) \equiv dN_{p,i}(\epsilon)/d\epsilon$ . The energy loss, in a material with specific mass  $\rho$ , depends upon its electron density and can be approximated, for  $\epsilon > 1$ , as:

$$-d\epsilon/dx = d\bar{\rho} \epsilon^{-0.8}, \quad (4)$$

where  $\bar{\rho} = \rho/(1 \text{ g cm}^{-3})$  and  $d = 2.6 \cdot 10^2 \text{ cm}^{-1}$  for most material but hydrogen ( $d_H = 6.5 \cdot 10^2 \text{ cm}^{-1}$ ). As a result, a particle with energy  $\epsilon_1$  will cross a hydrogen column density  $M_H^{col}$  and exit with an energy  $\epsilon_2$

$$\epsilon_2^{1.8} = \epsilon_1^{1.8} - 1.2 \cdot 10^3 M_H^{col}/(1 \text{ g cm}^{-2}), \quad (5)$$

if this quantity is positive, or will be absorbed if it is negative. If incoming protons have a spectrum  $\Phi_1(\epsilon)$ , the exiting spectrum,  $\Phi_2(\epsilon)$ , is,

$$\Phi_2(\epsilon_2) = \Phi_1(\epsilon_1) (\epsilon_2/\epsilon_1)^{0.8}, \quad (6)$$

$\epsilon_1$  and  $\epsilon_2$  being related by (5).

As anticipated, the flux coming in a straight line from the star to the icy region of the disk is completely negligible, even if there were no magnetic field. The H column density calculated from (1) and an inner radius of the disk  $r_{min} = 8 \cdot 10^{-2}$  ( $T =$

1 000 K), is  $M_H^{col} = 10^6 \text{ g cm}^{-2}$  or one ton per  $\text{cm}^{-2}$  ! Even protons with  $10^2 \text{ GeV}$  would be absorbed (Eq. (5)).

#### - Casual irradiation of pre-cometary grains

If some magnetic field lines were to penetrate into the disk what would be the irradiation of grains?

As grains condense towards the disk plane, they are protected from above and below by a layer of hydrogen gas. At the distance of Neptune's orbit, Eqs. (2) give a disk thickness corresponding to a column density  $M_H^{col}(30 \text{ AU}) = 2 \rho h = 10 \text{ g cm}^{-2}$ . We consider that all the grains are protected by a  $3 \text{ g cm}^{-2}$  layer of hydrogen as a minimum. Only impinging protons with a small pitch angle and initial energy  $E_1 > 70 \text{ MeV}$  can go through such a layer. We accept that 1% of the protostellar flux at that distance can penetrate into the disk with a small pitch angle although there is no evidence of such a process in the present models of preplanetary disks. Their spectra result from (3) and (6).

$$\Phi_2(\epsilon) = 8 \cdot 10^4 \epsilon^{0.8} (\epsilon^{1.8} + 3.6 \cdot 10^3)^{-1.9} \text{ cm}^{-2} \text{ s}^{-1}, \quad (7)$$

For a given grain, considered as a sphere with radius  $a$ , we assume that particles with energy  $\epsilon$  less than  $\epsilon_0$ , the energy corresponding to a mean path of protons in ice of  $2a$ , are stopped in the grains and the maximum production of  $\text{O}_2$  per incident proton is half the quantum yield of  $\text{H}_2\text{O}$  erosion or  $0.5 Y_{\text{H}_2\text{O}}(\epsilon)$ . For more energetic particles that traverse grains, we approximate the maximum production of  $\text{O}_2$  as half the product of the differential quantum yield by the grain diameter,  $0.5 dY/dx(\epsilon) 2a$ . An upper limit of that casual production of  $\text{O}_2$  is obtained by multiplying this yield by the impinging proton flux,  $\Phi_2(\epsilon)$ , the exposure duration,  $\Delta t$ , and summing over  $\epsilon$ :

$$N_{\text{O}_2} = \left( \int_0^{\epsilon_0} Y(\epsilon) dN_p/d\epsilon d\epsilon \right) + \int_{\epsilon_0}^{\infty} dY/dx 2a dN_p/d\epsilon d\epsilon \pi a^2 \Delta t. \quad (8)$$

The  $[\text{O}_2]/[\text{H}_2\text{O}]$  mixing ratio,  $x$ , is obtained by dividing  $N_{\text{O}_2}$  by the number of  $\text{H}_2\text{O}$  molecules in the grain,  $3.0 \cdot 10^{22} 4\pi(a/1\text{cm})^3/3$ . Using the preceding data, one finds:

$$[\text{O}_2]/[\text{H}_2\text{O}] < 1.3 \cdot 10^{-7} \text{ for grains smaller than } 10 \mu\text{m},$$

$6.5 \cdot 10^{-8}$  and  $6.5 \cdot 10^{-9}$  for icy bodies with radius 1 cm and 1m, respectively.

We conclude that even with overestimating assumptions, the production of  $\text{O}_2$  by high energy protons from the protostar in cometary grains is *minute* within the framework of present models of protostellar disks and winds.

## 5. Is there $\text{O}_2$ or $\text{O}_3$ in solar system comets?

An observational test of Noll et al.'s hypothesis is the presence of  $\text{O}_2$  and  $\text{O}_3$  in Solar System comets. At present *neither  $\text{O}_2$  nor  $\text{O}_3$*  has been detected, as parent species, in comets (Altwegg et al., 1993). An upper limit can be obtained as follows.

**Table 1.** Abundances taken into account in the model calculations

Molecule	Molecule abundance (in % of Water)
$\text{H}_2\text{O}$	100
CO	(a)
$\text{H}_2\text{CO}$	(a)
$\text{NH}_3$	1.3
$\text{CH}_3\text{OH}$	1.2
$\text{H}_2\text{S}$	0.25
$\text{CS}_2$	0.1
S	variable

During its encounter with Halley's comet, The High Intensity Sensor (HIS) of the Giotto Ion-Mass Spectrometer has measured in situ ions from mass 12 amu/e to 56 amu/e from ca. 130 000 km from the nucleus up to 1 300 km (Altwegg et al., 1993). Details on the HIS instrument and on the data analysis have been given elsewhere (Balsiger et al., 1987; Meier, 1988; Altwegg et al., 1993). Inside the ionopause the ion density at mass channel 32 is relatively low, at least compared to the two neighbouring masses 31 and 33, where the densities of protonated formaldehyde ions (mass 31) and protonated methanol ions (mass 33) respectively, are a factor of 5 higher than at mass 32.

The chemistry in the cometary coma has to be taken into account, to deduce, from ion densities measured in the coma, the abundance of the parent molecules in the nucleus. We use two different chemical models to determine the molecules that are responsible for the ions at mass/charge = 32 amu/e, one inside the ionopause surface, one outside, because the plasma parameters differ vastly between these two regions.

Inside the ionopause there is no interaction between the cometary plasma and the solar wind, the temperatures of molecules, ions and electrons are low (a few hundred K at most) and the outflow velocity of the ions and the neutral particles are equal and nearly constant ( $0.9 \text{ km s}^{-1}$ , Krankowsky et al., 1986). Assuming steady state flow conditions, the chemical model takes into account the relevant ion-molecule reaction rates, the photo rates (photoionization and photodissociation) and the electron recombination rates. The model used has been described by Geiss et al., 1991. Outside the ionopause the interaction with the solar wind is important and has to be taken into account (Häberli et al., 1995).

The molecules included in our modelling are listed in Table 1. Apart from the most abundant molecule,  $\text{H}_2\text{O}$ , we have also included extended sources (from grains in the coma) of formaldehyde and CO as described in Eberhardt et al.(1987), and point sources (comet nucleus) of  $\text{CO}_2$ , methanol and ammonia. We did not include molecules with low abundances which are of minor importance for the masses considered here.

(a) extended sources taken from Meier et al., 1993

The major ions which could contribute to the mass channel 32 apart from  $\text{O}_2$  are methanol ions,  $\text{S}^+$ , deuterated formaldehyde ions  $\text{H}_2\text{DCO}^+$ , and formaldehyde ions with  $^{13}\text{C}$ . We know from an analysis of the mass range 32 - 35 amu/e that the con-

**Table 2.** Reaction rates for O<sub>2</sub> molecules

Reaction	Rate (s <sup>-1</sup> )	Reference
Photodissociation O <sub>2</sub> + hν → O + O	67 10 <sup>-7</sup>	(a)
Photoionization O <sub>2</sub> + hν → O <sub>2</sub> <sup>+</sup>	12 10 <sup>-7</sup>	(a)
Electron recombination O <sub>2</sub> <sup>+</sup> + e <sup>-</sup> → O <sub>2</sub>	1.9 10 <sup>-7</sup>	(b)
Charge exchange H <sub>2</sub> O <sup>+</sup> + O <sub>2</sub> → H <sub>2</sub> O + O <sub>2</sub> <sup>+</sup>	1.2 10 <sup>-10</sup>	(c)

(a) Huebner et al., 1992

(b) Millar et al., 1991

(c) Anichic, 1993

tribution of S<sup>+</sup> inside the ionopause is minor (Altwegg et al., to be published).

To obtain an upper limit for O<sub>2</sub> inside the ionopause, we neglect the contribution from S<sup>+</sup> and formaldehyde and take only methanol ions into account. The methanol abundance has been determined earlier from mass 33, where the protonated methanol ions is present (Geiss et al., 1991). The reaction rates for oxygen species that determine the O<sub>2</sub><sup>+</sup> abundance are given in Table 2.

With these values, we obtain an *upper limit*, 0.5%, for the abundance of O<sub>2</sub> parent molecules relative to water which is representative of the cometary nucleus abundance. As mentioned, this value neglects sulphur and formaldehyde which are both present in the comet and may be the major contributors to mass 32. The actual value of O<sub>2</sub> abundance is therefore probably *much lower* than the 0.5% deduced here. A more detailed analysis of the deuterium content in formaldehyde and a comparison with the data from the Neutral Mass Spectrometer of Giotto should lead, in the future, to a more precise value for O<sub>2</sub>. However, the present upper limit is already lower than the value postulated by Noll et al. (1997) (a few percent).

Another piece of evidence of the very low content of comets in oxygen is provided by the study of Pluto and Triton. We do not find abundant O<sub>2</sub> on the surface of these two objects that must have accreted from icy planetesimals. We DO find CH<sub>4</sub>. If there were large amounts of O<sub>2</sub> in the icy planetesimals (comets) that formed these bodies and that continue to impact them, wouldn't we expect this CH<sub>4</sub> to become CO<sub>2</sub>? CH<sub>4</sub> is a minor constituent in comets and in the ISM. Thus its presence on Pluto and Triton is itself a bit of a puzzle. Perhaps it is made by impacts, but this again would be impossible if abundant O<sub>2</sub> were present.

Whenever a telluric planet is young and large enough to still have volcanism, the O<sub>2</sub> input by cometary impacts has to be high enough to overcome the efficient sink that results from the action of reducing rocks and gases from volcanoes, to build a O<sub>2</sub> rich atmosphere. The low oxygen content of comets, if any, does not favour such a high input.

In summary, the hypothesis of O<sub>2</sub> being present in comets has *no observational support* in the present Solar System.

## 6. Are invoked processes contingent to the solar system or generic?

The main argument in favour of the generic nature of the processes invoked is that they result from general physics and chemistry laws.

A basic assumption is that carbon is mainly present on telluric planets in its fully oxidised state (CO<sub>2</sub> or carbonates) and that its greenhouse effect leads to a moderate climate on the planet. The first point results from the chemical equilibrium between CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O and H<sub>2</sub> gases. Regarding the second point, telluric planets are searched for around neighbouring stars whose metallicity will be measured, and is expected to be similar to that of the Solar System within a factor of a few. CO<sub>2</sub> or carbonates should be abundant on these planets, providing, if plate tectonics is present, the climate regulation process that has been described for planets in the CHZ. Indeed, the proposed IR missions will be able to check whether CO<sub>2</sub> is actually present in the atmospheres thanks to the measurement of the 15 μm band.

Plate tectonics and volcanism also play a key role by providing an efficient sink for free O<sub>2</sub>. They are the result of internal planet heating by radioactive uranium, and of silicate fluidity enhanced by hydration and are expected to be generic whenever the mass of the planet is sufficient and liquid water is present on it. The presence of H<sub>2</sub>O will also be determined by the missions (absorption in the 6-8 μm range). The size of the (possibly) detected telluric exoplanets, and an estimate of their mass, can be determined as follows. The shape of the IR spectrum will yield the effective temperature of the emitting atmosphere and the absolute IR flux will yield its area, provided a sensible assumption is made of the planet's IR emissivity. Then, for planets of the size of, or larger than, the Earth, located in the CHZ and with spectroscopic evidence of H<sub>2</sub>O, the occurrence of plate tectonics and volcanism is expected as generic processes.

## 7. Conclusion

Noll et al. (1997) have not stated that the O<sub>3</sub> criterion was incorrect, they have stated that *if* comets contain few percents of free O<sub>2</sub> per mass, their impacts on telluric planets would be an appreciable source of abiotic O<sub>2</sub> and O<sub>3</sub>. They have proposed a mechanism for the presence of such species in comets: the chemical reactions induced by particle irradiation on pre-cometary icy grains.

We have shown that recent models of protoplanetary disks actually do not predict the production of a significant amount of O<sub>2</sub> in comets. Though these models cannot be considered as final, their quality is indicated by their ability to predict several independent intriguing features observed in the Solar System (Shu et al. 1997).

In addition, Noll et al.'s hypothesis has no observational support in the Solar System:

- (i) neither O<sub>2</sub> nor O<sub>3</sub> has been detected in comets (upper limit: [O<sub>2</sub>]/[H<sub>2</sub>O] < 0.5 % for Halley's comet)
- (ii) the O<sub>2</sub> input that would have resulted on the Young Earth,

when cometary bombardment was heavy, did not build an oxygen rich atmosphere.

We conclude that the simultaneous detection of significant amounts of H<sub>2</sub>O and O<sub>3</sub> (corresponding to an O<sub>2</sub> pressure larger than 10 mbar, Léger et al. 1993b) in a telluric exoplanet, with a size comparable to, or larger than, that of the Earth and located in the Continuously Habitable Zone of its star presently stands as a criterion for a large *photosynthetic* activity on a planet (see also Kasting, 1997).

Now, is this a real signature of a *biological* process? For G or later type stars, in the presence of a UV shielding by the planetary atmosphere, e.g. by O<sub>2</sub> and O<sub>3</sub>, photosynthesis requires the absorption of several stellar photons and the storage of energy in between. A system that is able to do so has to be so complex a "factory" that it is difficult not to think of it as the result of a biological evolution (Raulin, private comm.).

Considering the fact that the H<sub>2</sub>O - O<sub>3</sub> criterion is considered as a criterion for remote detection of life (and is the base of most present mission concepts developed to achieve this goal), it is highly desirable to keep on developing a continuous and vigorous conceptual and modelling activity, in order to qualify or falsify it.

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