$O^{\bullet}$, O_2 and O_3: the key to life on the Earth

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Abstract $O^{\bullet}$, O_2 and O_3 play vital roles in the Earth's atmosphere, regulating ultraviolet radiation from the Sun and being essential for life. However, the oxygen family, $O^{\bullet}$, O_2 and O_3, also provides a source of the HO radical, the atmospheric detergent that removes pollutants from the atmosphere. This article also discusses the decline in oxygen levels that have been observed and the latest data that suggest that the stratospheric ozone hole is recovering.

The role of molecular oxygen (O_2) in the existence of life on planet Earth is well known but its allotropes, atomic oxygen ($O^{\bullet}$) and ozone (O_3) are key to life on present-day Earth as well. It is debated who discovered molecular oxygen, Lavoisier or Priestley (Sukopp, 2018), but we know from palaeoclimate data that for over 200 million years elevated levels of oxygen have been present in the atmosphere and that it constitutes around 21% of the Earth's present-day atmosphere. The source of oxygen in the atmosphere is from the process of photosynthesis (equation 1). The endothermic process utilises energy from the Sun ($h\nu$) to convert carbon dioxide (CO_2) and water (H_2O) into sugars ($C_6H_{12}O_6$), which the organism uses as a source of energy with the waste product being oxygen:

$$6CO_2 + 6H_2O + h\nu \rightarrow C_6H_{12}O_6 + 6O_2 \qquad (1)$$

However, the consumption of oxygen is mainly through the combustion of fossil fuels (25.02 Gt/year) and biomass burning (5.87 Gt/year), depicted in general by equation 2, with contributions from human respiration (3.09 Gt/year) and livestock respiration (2.24 Gt/year) (Huang *et al.*, 2018):

$$CxHy + (x + (y/4))O_2 \rightarrow xCO_2 + (y/2)H_2O \qquad (2)$$

where the sources of oxygen are plants (16.01 Gt/year) and algae (1.74 Gt/year) (Huang *et al.*, 2018).

It has been shown that CO_2 levels are rising, so we would then expect the level of O_2 to be dropping. Indeed, it has been observed in recent times that, as CO_2 levels have risen, so O_2 levels in the atmosphere have been declining (Figure 1). However, decline in the levels of O_2 is inferred from analysis of air bubbles trapped in the ice in the polar regions for many years. Such analyses suggest that the decline (0.7%) has been taking place for much longer (*c.* 800 000 years) and there is no one clear reason for this (Stolper *et al.*, 2016). Increased rates of erosion or weathering are possible reasons: as minerals are exposed they are oxidised, removing oxygen from the atmosphere. The more rapid glacial to inter-glacial cycles in the last 500 000 years may also be a reason for increased erosion rates. Another possible reason is the long-term cooling of the planet's surface since the PETM (Palaeocene–Eocene Thermal Maximum) some 56 million years ago. Cooler oceans can hold more molecular oxygen and this may be another reason for the decline. Changes in biodiversity, volcanic activity and other Earth-system processes may also play a

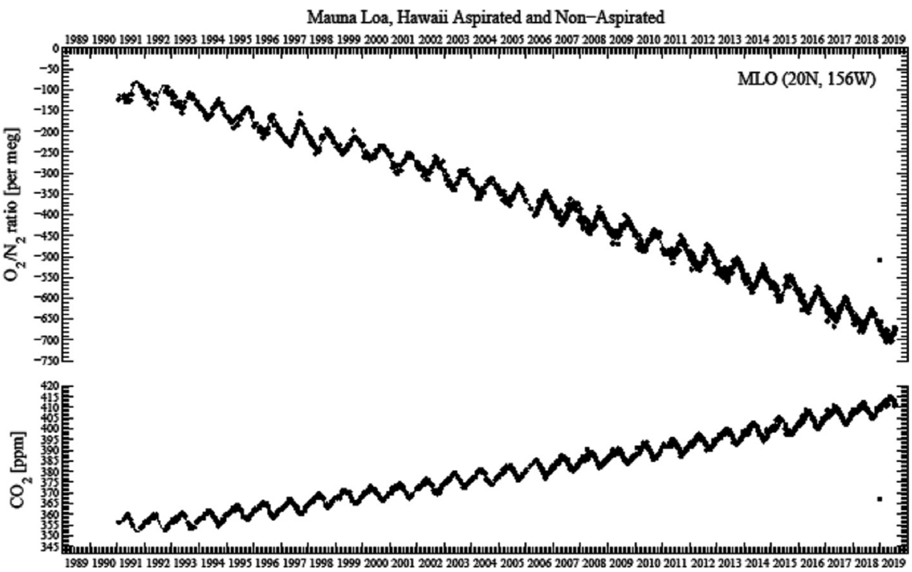

Figure 1 Changes in levels of atmospheric CO_2 and O_2 from 1990 to 2019 in the northern hemisphere (Mauna Loa Observatory, Hawaii); the O_2 concentrations are shown as relative changes in O_2/N_2 ratio and CO_2 concentrations in ppm units; plots adapted from Scripps Institution of Oceanography: http://scrippso2.ucsd.edu

role; this is an unsolved question in Earth-system science at present.

Has oxygen always been at the level it is today? It has not. Through analysis of mass-independent fractionation of sulfur isotopes in sediments, the levels of oxygen are shown to have varied significantly over the last *c.* 2.4 billion years, following the so-called 'Great Oxidation Event', when oxygen levels first started to build in the Earth's atmosphere (Papineau, Mojzsis and Schmitt, 2007). During the Carboniferous period (*c.* 300 million years ago), oxygen levels were at their height, at approximately 35% (Figure 2).

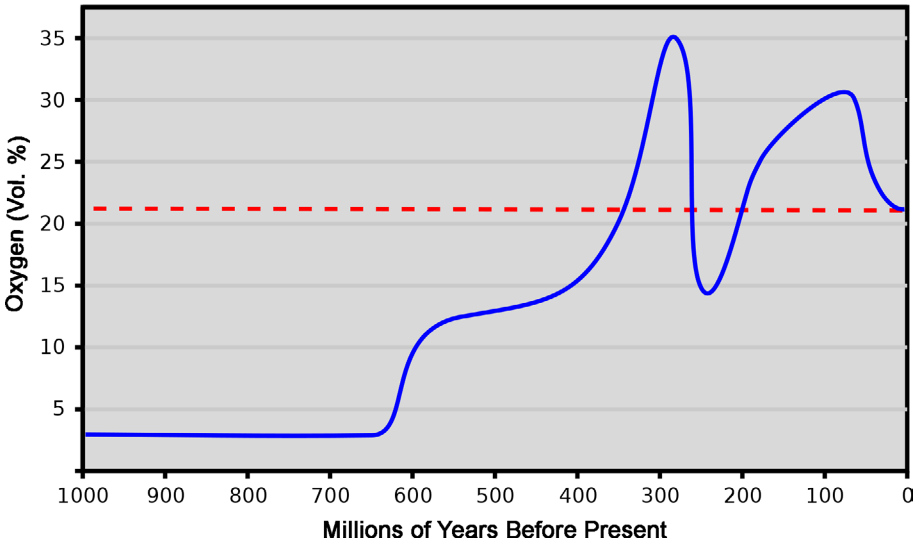

Figure 2 Changes in levels of O_2 during Earth's history; image in the public domain, from https://commons.wikimedia.org/wiki/File:Sauerstoffgehalt-1000mj2.png

Once oxygen was present in the atmosphere, the formation of its allotrope ozone (O_3) was possible. Ozone was first discovered by Christian Friedrich Schönbein in 1839 (Leeds, 1879), and in 1930 Sydney Chapman showed that the ozone layer (a region in the atmosphere that is rich in ozone between 10 and 50 km above the Earth's surface) resulted from the following four reactions (Chapman, 1930):

$$O_2 + h\nu \rightarrow O^\bullet + O^\bullet \quad (3)$$

$$O^\bullet + O_2 + M \rightarrow O_3 + M \quad (4)$$

$$O_3 + h\nu \rightarrow O_2 + O^\bullet + \text{heat} \quad (5)$$

$$O^\bullet + O_3 \rightarrow 2O_2 \quad (6)$$

Reaction 3, the photolysis of oxygen, requires photons of light in the vacuum UV (around 200 nm) and is most efficient in the upper atmosphere, where high-energy photons from the Sun are most prevalent. Reaction 3 produces O atoms that can then combine with oxygen molecules to make ozone. However, the newly formed ozone molecule will have a lot of energy located in the new O–O bond formed and needs to be stabilised by collisions with N_2 and O_2 molecules in the atmosphere. These collisions remove energy and as the number density (M, number of molecules per m^3) decreases with altitude, reaction 4 becomes less efficient as altitude increases. Therefore, the two reactions that are needed to form ozone are at a maximum at totally different altitudes. It turns out that the ozone layer, the region where the production of ozone is at its largest, is between 10 and 50 km, that is, somewhere in the middle. Molecular oxygen and ozone act as a perfect screen to harmful UV radiation from the Sun, protecting the surface of the Earth. The stratosphere, where the ozone layer resides, is a warm layer of the atmosphere, where temperature rises with altitude through reaction 5. The photolysis of ozone, the absorption of a vacuum UV photon (around 250 nm) by ozone, is a highly exothermic reaction. The warm layer of air in the stratosphere moderates weather in the troposphere (lowest 10 km) and helps to make the surface of the Earth more habitable.

However, this is not the whole story: there are natural catalysts that speed up reaction 6. These include $^\bullet$NO, $H^\bullet$, $HO^\bullet$, $Cl^\bullet$ and $Br^\bullet$, which take part in a two-step catalytic cycle:

$$X^\bullet + O_3 \rightarrow XO^\bullet + O_2 \quad (7)$$

$$XO^\bullet + O \rightarrow X^\bullet + O_2 \quad (8)$$

The sources of these natural catalysts are summarised in Table 1 and include water, methane and nitrous oxide, molecules that are present in the biosphere and not dependent on human activity.

Table 1 Sources of naturally occurring catalysts

$X^\bullet$	$XO^\bullet$	Source
$NO^\bullet$	NO_2	N_2O
$H^\bullet$	$HO^\bullet$	H_2O/CH_4
$HO^\bullet$	$HO_2^\bullet$	H_2O
$Cl^\bullet$	$ClO^\bullet$	CH_3Cl
$Br^\bullet$	$BrO^\bullet$	CH_3Br

Ozone hole: its recovery

The role played by CFCs (chlorofluorocarbons) in the generation of the ozone hole over the Antarctic is well documented and was summarised by us in a previous article (Shallcross and Harrison, 2010). Banning of these CFCs and the use of short-term replacement compounds such a HCFCs (hydrochlorofluorocarbons), which have a small ozone depletion potential, and HFCs (hydrofluorocarbons), which do not destroy ozone at all, has reduced the amount of Cl and Br present in the stratosphere and data now suggest that the ozone hole is recovering (Figure 3), with both the ozone minimum increasing and the area of the ozone hole decreasing. However, we need to keep monitoring the situation, as recent research found that $CFCl_3$ (trichlorofluoromethane) was being used illegally in China (Rigby *et al.*, 2019). Apart from increasing the level of harmful radiation that we would have been exposed to at the surface of the Earth, the CFCs are potent greenhouse gases with a long lifetime. Therefore, if we had not banned their use we would have also accelerated global warming dramatically.

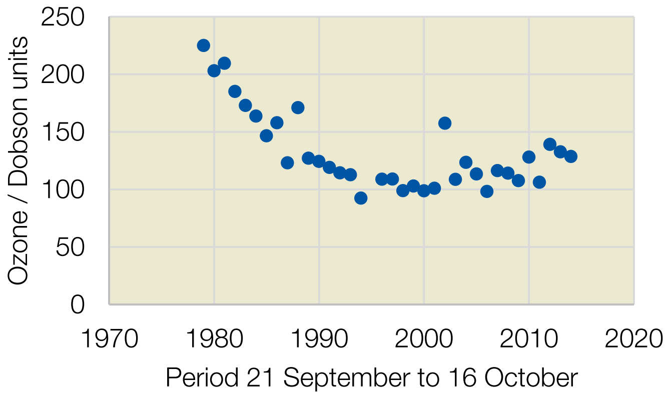

Figure 3 Minimum ozone levels (in Dobson units) between 21 September and 16 October each year over the Antarctic; data from NASA Ozone Watch (https://ozonewatch.gsfc.nasa.gov/meteorology/ozone_1980_MERRA_SH.html)

Atomic oxygen and the HO• radical

In the lower atmosphere, known as the troposphere, HO• radicals are an essential cleaning agent, reacting with most pollutants (apart from CFCs that are inert), and are formed by the photolysis of ozone, as in the stratosphere where some of the O atoms formed are excited (denoted as O*):

$$O_3 + h\nu \rightarrow O_2 + {}^{\bullet}O^* + \text{heat} \quad (5)$$

Excited O* atoms can then react with water vapour to form HO• radicals:

$$H_2O + {}^{\bullet}O^* \rightarrow HO^{\bullet} + HO^{\bullet} \quad (9)$$

Therefore, the highest levels of HO• are typically found in places that receive high levels of sunlight and have high levels of humidity; that is, the tropics. For pollutants to enter the stratosphere (the layer above the troposphere), they need to pass through the tropical region and so the Earth system has an excellent system to prevent pollutants from entering the stratosphere. The CFCs were the exception and caused the ozone hole.

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