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Global oceanic and atmospheric oxygen stability considered in relation to the carbon cycle and to different time scales

Oxygen
Carbon dioxide
Air-sea exchange
C_3/C_4 photosynthesis
Global change

Oxygène
Dioxide de carbone
Échange air-mer
Photosynthèse C_3/C_4
Changement global

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ABSTRACT

This paper constitutes an overview and synthesis concerning atmospheric and oceanic oxygen and related carbon dioxide, particular attention being paid to potential regulation mechanisms on different time scales. The world atmospheric oxygen reserve is remarkably large, so that a lack of oxygen will not easily occur, whether in confined spaces or in major conurbations. On "short" scales, measured in hundreds or thousands of years, feedback processes with regard to oxygen regulation, solely based on atmospheric oxygen variations, would have to be so highly sensitive as to be barely conceivable. Only oxygen in the oceans can vary between zero and about twice the saturation - a fact which suggests that here, at least potentially, there exist possibilities for a feedback based on oxygen changes.

Atmospheric oxygen production began some 3.2 billion years ago, and has resulted in a net total amount of 5.63×10^{20} mol (1.8×10^{22} g) of oxygen, of which 3.75×10^{19} mol is present as free oxygen in the atmosphere and 3.1×10^{17} mol as dissolved oxygen in the oceans, the remainder being stored in a large number of oxidized terrestrial and oceanic compounds. For the past 600 million years, atmospheric oxygen has been modelled as ranging between 7 and 30 O_2 vol % (one model even proposes up to 35 O_2 vol %).

The present global atmospheric oxygen level remains remarkably constant at a level of 20.946 ± 0.006 vol %, with a slight decrease of 0.0004 O_2 vol %/yr (4 ppmv/yr) which is counter-correlated to CO_2 produced by fossil-fuel and biomass burning. Burning of all terrestrial biomass and humus will potentially reduce oxygen to 20.846 O_2 vol %, while combustion of all known fossil fuel reserves will eventually stabilize oxygen at 20.104 O_2 vol %. The present increase in atmospheric CO_2 of about 2 ppmv/yr is linked to a global warming of 0.0125 °C/yr, at least in higher latitudes. A similar annual rise in ocean temperature will lead to a release of between 0.2 and 0.5 %/yr of the oxygen present there, and the oceanic oxygen system can be considered as sensitive to global heating.

On a small time scale, oxygen is negatively correlated on a 1:1 basis to atmospheric CO_2, which is at the level of 0.03 vol % or 300 ppmv (1965 level; 1992 level: 360 ppmv). Thus, close to vegetation, atmospheric oxygen cannot increase by more than this amount (0.03 vol %), and can therefore not exceed 20.976 vol %. The chance of an increase in forest fires due to oxygen variations is consequently negligible.

The atmosphere-ocean exchange budget of CO_2 is dominated by the fossil-fuel and biomass fire-derived CO_2, of which 39 % is due to CO_2 increase in the atmosphere, 30 % is taken up by the oceans, the remainder possibly being recovered by biomass growth. Compared to the atmosphere-ocean flux of CO_2, the biogenic ocean fluxes of carbon ("oceanic biological pumps") are lower by a factor of at least ten (burial of organic matter and foraminifers, and reef growth).

Feedback processes of regulation of atmospheric oxygen related to photosynthesis-respiration are difficult to prove for "short" periods counted in hundreds or thousands of years, but may be linked to shifts in C_3/C_4 photosynthetic activities both on land and in the sea. C_3 and C_4 photosynthetic pathways react differently to changing environmental conditions such as light, temperature, moisture (on land), CO_2 and O_2 levels and nutrients. C_4 photosynthesis is more efficient than that of C_3 with respect to nutrients. At higher temperatures, C_4 photosynthesis is favoured on land and possibly also in the sea. The environmental impact on feedback is discussed in relation to different time scales, and with reference to the earth, its oceans and ocean margins, glacial and interglacial periods, for which the potential contribution by the oceans to the control of atmospheric oxygen changes is evaluated.

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RÉSUMÉ

Stabilité planétaire de l'oxygène océanique et atmosphérique et son implication avec le cycle du carbone à différentes échelles de temps

Cette revue bibliographique commentée traite de l'oxygène atmosphérique et océanique ainsi que de ses relations avec le dioxyde de carbone. Elle met l'accent sur les mécanismes potentiels de régulation pour les différentes échelles de temps. La réserve atmosphérique d'oxygène est si grande qu'elle est suffisante, même dans des espaces réduits et dans les grandes villes. Ainsi, à court terme (centaines ou milliers d'années), les mécanismes de régulation de la teneur atmosphérique en oxygène fondés seulement sur ses variations dans l'atmosphère doivent être très sensibles, puisque ces variations sont très difficiles à mesurer. Il n'y a que les teneurs en oxygène des océans qui peuvent varier dans de larges proportions, entre zéro et deux fois la valeur de saturation, offrant ainsi, au moins en théorie, une possibilité de régulation fondée sur ces variations.

La libération de l'oxygène dans l'atmosphère a commencé il y a 3,2 milliards d'années et a, depuis, produit $5{,}63 \times 10^{20}$ mol ($1{,}8 \times 10^{22}$ g) d'oxygène qui se répartissent en $3{,}75 \times 10^{19}$ mol d'oxygène sous forme libre dans l'atmosphère et $3{,}1 \times 10^{17}$ mol d'oxygène dissous dans les océans, le reste étant stocké dans la terre et les océans sous la forme de multiples composés oxydés. Au cours des derniers 600 millions d'années, l'évolution des teneurs en oxygène de l'atmosphère a été simulée par des modèles mathématiques qui montrent des variations comprises entre 7 et 30 % en volume (un modèle donne jusqu'à 35 % en volume). Le niveau actuel de l'oxygène atmosphérique est remarquablement stable à 20,946 ± 0,006 % en volume, avec seulement une légère diminution de cette teneur de 0,0004 %/an en volume (4 ppmv/an). Cette diminution est inversement corrélée à l'augmentation du CO_2 due à la combustion des hydrocarbures fossiles et de la biomasse végétale des savanes et en raison des pratiques de déforestation. La combustion de toute la biomasse terrestre et de l'humus réduirait la teneur en oxygène atmosphérique à 20,846 % en volume ; de même, celle de toutes les réserves connues en hydrocarbures fossiles stabiliserait cette teneur à 20,104 % en volume. L'augmentation actuelle du CO_2 atmosphérique d'environ 2 ppmv/an se traduit par un accroissement mondial de la température de 0,0125 °C/an, au moins pour les hautes latitudes. Cette augmentation de température doit avoir comme conséquence pour les océans une perte de 0,2 à 0,5 % de son oxygène par an. Ainsi le contenu en oxygène des océans doit être considéré comme très sensible aux changements mondiaux des températures.

Pour de courtes échelles de temps, la teneur en oxygène atmosphérique est inversement corrélée, sur la base de 1:1, avec celle du CO_2 qui est de 0,03 % en volume ou 300 ppmv (valeur de 1965 et 360 ppmv actuellement). Ainsi, à proximité immédiate de la végétation, la concentration en oxygène atmosphérique ne peut augmenter de plus de 0,03 % en volume, et de ce fait ne peut pas dépasser 20,976 % en volume, ce qui exclut un départ spontané des feux de forêts, dû aux variations des concentrations en oxygène. Le bilan des échanges de CO_2 entre l'océan et l'atmosphère est actuellement dominé par le CO_2 produit par la combustion des hydrocarbures fossiles et de la biomasse végétale dont 39 % conduisent à une augmentation du CO_2 de l'atmosphère, et 30 % se dissolvent annuellement dans les océans, le reste pouvant être récupéré par une augmentation de la biomasse annuellement produite. En comparaison de ce flux entre l'atmosphère et l'océan, tous les flux océaniques biogènes de carbone («oceanic biological pumps») sont au moins dix fois plus faibles (enfouissement de la matière organique dans les sédiments, construction des récifs coralliens et fixation par les foraminifères).

Les régulations de la teneur atmosphérique en oxygène fondées sur la relation photosynthèse-respiration sont difficiles à démontrer pour des périodes «courtes» de 100 à 1 000 années, mais peuvent probablement être reliées à des changements dans les activités photosynthétiques des végétaux de type C_3 et C_4, aussi bien sur terre qu'en mer. Les cycles C_3 et C_4 d'assimilation du CO_2 par les végétaux réagissent différemment aux changements des conditions de l'environnement telles que la lumière, la température, l'humidité (sur terre) et les concentrations en CO_2, O_2 et sels nutritifs. Le cycle photosynthétique en C_4 est plus efficace que celui en C_3 pour une même quantité de sels nutritifs. A haute température, le cycle C_4 est favorisé sur terre et probablement aussi en mer. L'impact de l'environnement sur ces régulations est discuté en tenant compte de leurs échelles de temps pour la planète, les océans et les interfaces continents-océans ; puis pour les périodes glaciaire et interglaciaire. Les contributions potentielles des océans dans le contrôle de l'oxygène atmosphérique sont ainsi estimées.

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INTRODUCTION

In a great number of scientific and political discussions on "Global Changes", which generate a large amount of funds for research, the term "Global Stability" is usually absent. This is remarkable since these changes occur within a system that demonstrates in many aspects an extraordinary stability, on which they are merely superimposed. Oxygen is a major and essential element for the existence of life on earth. It is related to carbon dioxide and water for both its production during photosynthesis and assimilation during respiration. Nevertheless in these discussions on global changes, atmospheric oxygen receives scant attention, apart from statements that, e. g., tropical forests are the "lungs' of the earth, suggesting that these forests are of essential value for the level of oxygen in the earth's atmosphere. A few publications clearly state that the pool of atmospheric oxygen is very largely sufficient to sustain life on earth for very long periods (Berkner and Marshal, 1965; 1966; Broecker, 1970; Walker, 1980; Budyko *et al.*, 1987). Broecker (1970) calculated that a complete combustion of all known reserves of fossil fuel would not reduce the oxygen level by more than 3 out of 100 molecules of oxygen from the present level of about 21 vol %.

The level of atmospheric oxygen also seems very stable when measured over a number of years, as was determined by Machta and Hughes (1970). Between 1967 and 1970, the atmospheric oxygen between 50 ° and 60 °S had an almost constant value of 20.946 ± 0.006 vol %. These findings on its global stability explain why only a limited literature exists on atmospheric oxygen. But on the other hand they also raise a number of questions:

Why is this reserve of atmospheric oxygen so large?

Why is the oxygen level apparently stable at 20.946 vol %?

What is the role of the oceans in this aspect?

Is there a loss of oxygen to space?

What are the world (ocean and terrestrial) feedback processes of O_2 and CO_2 that regulate the apparent oxygen equilibrium?

On what time scales do these processes occur?

In this paper we endeavour to provide some answers to these questions.

PREHISTORIC ATMOSPHERIC OXYGEN LEVELS

The creation of oxygen in the earth's atmosphere (*see* also Holland, 1984; Broecker, 1985; Kasting, 1993) is considered by Rutten (1970) to have taken place in three stages:

Urey level, more than 3.2 billion years ago

Formation

Oxygen in the very prehistoric atmosphere is believed to have been formed from water molecules through dissociation. At high altitudes, powerful UV radiation from space caused dissociation of H_2O vapour (1), followed by a secondary reaction involving the formation of ozone (O_3) from O_2 (2).

$$2H_2O \Leftrightarrow 2H_2 + O_2 \qquad (1)$$

$$3O_2 \Leftrightarrow 2O_3 \qquad (2)$$

Feedback

The level of oxygen is kept stable by the following feedback process: UV radiation is reduced through absorption by the ozone produced, thus also reducing the formation of oxygen from water. The equilibrium level thus obtained is estimated to be 1/1 000 of the actual level, *i. e.*, about 0.02 O_2 vol %. Whether this O_2 level is completely correct is a matter of discussion. For example, Canuto *et al.* (1982) suggest that the UV output from the "young" sun was at that time considerably higher than the present-day UV radiation level. They base this fact on studies of comparable young T-Tauri stars. On the other hand, Cloud (1974) maintains that the oxygen produced was easily consumed by the reductive gases "outgassed" from the earth. These consumers certainly existed but they do not interfere with the feedback process.

Pasteur level, from 3.2 to 1.8 billion years ago

Formation

According to Rutten (1970), an initial form of primitive photosynthesis producing oxygen began approximately 1.8 billion years ago. He based this on the dating to that time of the oldest oxidized sediments containing, in particular, trivalent iron (Schidlowski, 1980).

Feedback

Oxygen was still consumed by volcanic gases, in particular hydrogen, but when the atmospheric oxygen increased to a level ten times that of the UV-produced oxygen, microorganisms, which decompose organic matter below this level by fermentation (anaerobic respiration), started to switch to aerobic respiration, thereby stabilizing the atmospheric oxygen at 0.2 O_2 vol %. The level at which this occurred is called the "Pasteur level" (0.01 PAL = 0.01 times the Present Atmospheric Level).

Oxygen from 1.8 billion years ago to present

Formation

About 1.8 billion years ago, photosynthesis started using chlorophyll pigments. This occurred first in water systems below a water column of about 10 m, out of reach of the continued high level of hazardous UV radiation, which was absorbed by this water layer. Later, when sufficiently high levels of atmospheric O_2 and consequently of ozone (according to formula 2), were built up, this ozone absorbed the major part of the hazardous UV radiation. As a result, photosynthesis manifested itself in surface waters and on land. The level of oxygen settled finally at 20.946 O_2 vol % in most recent times.

Feedback

The major feedback systems, capable of stabilizing oxygen at 20.946 vol % over time scales of thousands of years, are not known, but should be related to the balance between photosynthesis (production of oxygen) and respiration (use of oxygen) on the one hand, and the oxidation of reduced products such as Fe(II) compounds on the other hand (Kump and Holland, 1992). The process that results in additional oxygen is the burial of organic matter, while weathering of buried organic matter will again consume O_2. On the basis of rates of burial and weathering of organic carbon, Budyko *et al.* (1987), Berner and Canfield (1989) and Kump (1992; 1993) obtained conflicting modelling results on oxygen fluctuations for the period of 600 million years ago until the present day. Their differences mainly concern the periods of maximum and minimum atmospheric O_2. The basis for their models is given by Garrels and Perry (1974) in formula (3).

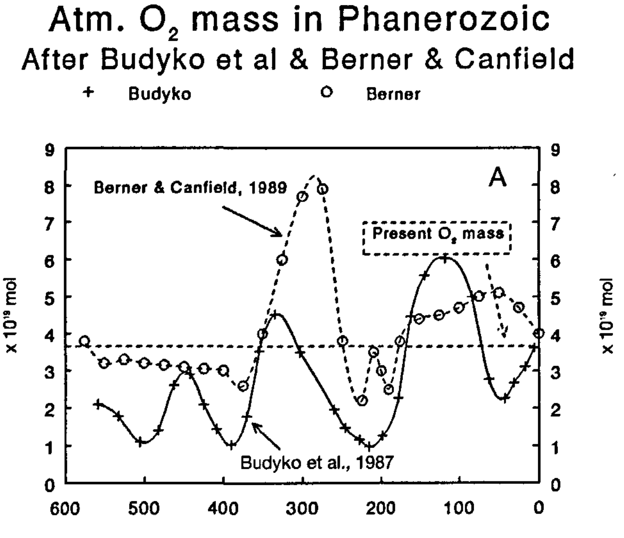
$$\begin{aligned}&15CH_2O + 8CaSO_4 + 2Fe_2O_3 + 7MgSiO_3\\ &\Leftrightarrow 8CaCO_3 + 4FeS_2 + 7MgCO_3 + 7SiO_2 + 15H_2O \qquad (3)\end{aligned}$$

which is a linkage of oxidized reservoirs ($CaSO_4$, Fe_2O_3, $CaCO_3$) and reduced reservoirs (FeS_2, CH_2O), where CH_2O is organic matter. This formula is the basis for the BLAG model worked out by Berner *et al.* (1983). Atmospheric oxygen can remain stable when CH_2O is balanced by FeS_2, *i. e.* a diminution of CH_2O should be accompanied by a diminution of FeS_2 (Kump, 1993). In geological records this is not fully the case. The implication of uncoupled behaviour of organic matter and pyrite (FeS_2) gives excessive fluctuation in the atmospheric oxygen content through the rapid photosynthesis-respiration reaction given in formula (4, above), in which there is a one-to-one molecular (and vol %) correlation between CO_2 and O_2. Shifts from burial of marine (-C and -S-coupled) organic carbon to terrestrial (only -C-coupled), also exist.

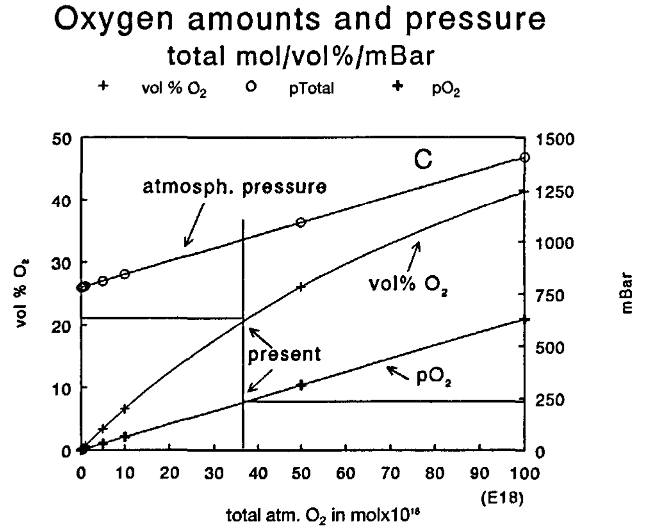
$$\begin{aligned}&CO_2 + H_2O \Leftrightarrow CH_2O + O_2 \text{ (fast)} \qquad (4)\\ &\updownarrow\\ &CO_2 + 2H_2O + CaAl_2Si_2O_8\\ &\Leftrightarrow Al_2Si_2O_5(OH)_4 + CaCO_3 \text{ (million years)}\end{aligned}$$

Parallel to the (4, above) reaction there occurs the chemical weathering of Ca-Mg silicate rocks (4, below), whereby on a million-year time scale CO_2 is removed from the atmosphere (Berner *et al.*, 1983; Berner, 1992). Thus, in the overall reaction, CO_2 is equally involved in another loop and on the long time scale, δCO_2 is not equal to δO_2. This reaction is supposedly enhanced by vascular land plants due to their capacity of secreting acids and recycling water (Berner, 1992). The reverse reaction, in which CO_2 is liberated, occurs through metamorphism and magmatism, and is modelled by Berner (1991).

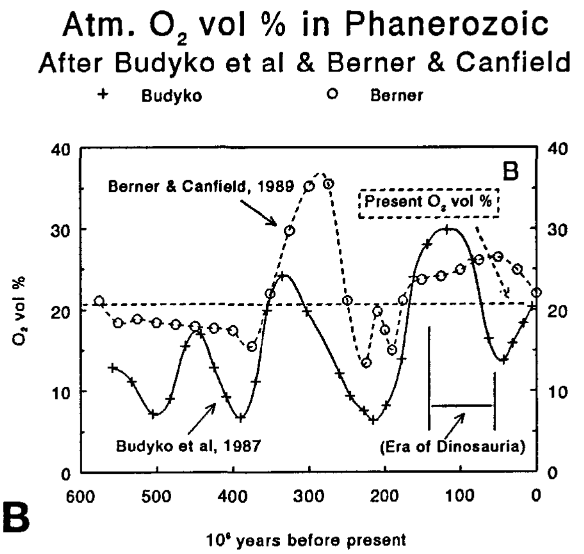
The results of the atmospheric oxygen model of Budyko *et al.* (1987) and Berner and Canfield (1989) are given in Figure 1 A. Where Budyko *et al.* present a sinusoid curve, with increasing maxima, Berner and Canfield present a much more irregular pattern, with a large peak at 300 million years ago. This maximum is very surprising, since the peak corresponds to 35 vol % of O_2 in the atmosphere, as



A



C



B

Figures 1 A, B and C

A: Response of total atmospheric oxygen reserve to the carbon-sulphur-phosphorus biogeochemical model from now until 600 million years ago, after Budyko et al. *(1987) and Berner and Canfield (1989). Data reproduced by permission of Springer-Verlag and the American Journal of Science, respectively.*

B: Ibid. *but calculated with the use of Figure 1 C in O_2 vol %. The O_2 vol % = [(mol O_2)/(Σ mol O_2 + N_2 + Ar)] x 100%. The peak at -300 million years ago corresponds to 35 vol % O_2.*

C: Correlation between the total O_2 atmospheric reserve with the O_2 vol %, the atmospheric pressure and pO_2. For this calculation it is supposed that the molecular reserve of $\Sigma(N_2$ + Ar + other gases) remains essentially the same (Holland, 1978; 1984) and CO_2 = 0.03 vol %.

can been seen from Figure 1 B. The vol % data are calculated from Figure 1 A, using the relationship between total oxygen mass and vol %, given in Figure 1 C. Whether large changes in oxygen level might have had effects on animal life, such as dinosauria, is discussed by Duursma and Boisson (1993).

As Watson *et al.* (1978) inferred, high oxygen levels should increase the probability of forest and grass fires. The immediate question which then arises is which vegetation type may have produced extremely high levels of oxygen and at the same time escaped conflagration? High atmospheric oxygen can only be caused in the absence of fires, privileging high primary productivity over respiration. To reduce chances of ignition at such high oxygen levels, the climate must have been very humid. On the other hand, this oxygen may have been produced by the oceans. In periods of warm climates, such as the early Cretaceous, black-shale formation took place (de Boer, 1986) and oxygen excess production (over respiration) occurred when the deep ocean was partially anoxic. In these deep basins, excess burial of organic matter contributed to the imbalance between oxygen production (in surface layers by photosynthesis) and respiration (over the complete column).

PRESENT OXYGEN RESERVES

Amount of O_2 and CO_2 present in the atmosphere and oceans

ATMOSPHERE

Oxygen

A calculation of the amount of O_2 in a column of atmosphere per unit surface of 1 m^2 on land and sea is easy to make. Broecker (1970) used the method of weight (pressure)/m^2 earth surface, while a calculation is also possible by using the pressure as function of height (Fig. 2), not taking into account mean continental elevation.

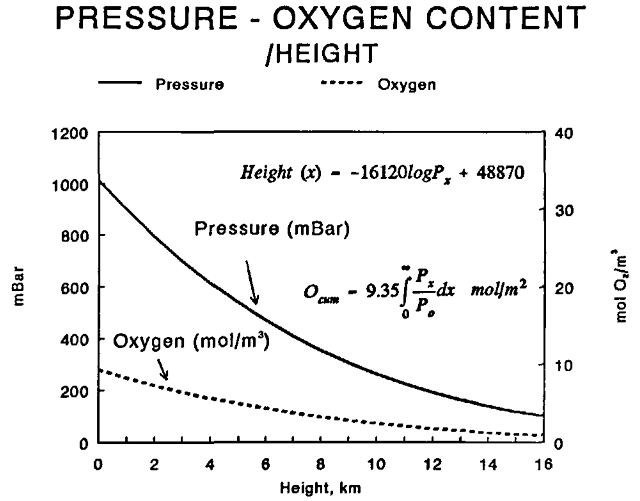


Figure 2

Atmospheric pressure and O_2 as functions of height, where O_{cum} = the cumulative oxygen from sea level to a height of x metres, P_o = atmospheric pressure in mBar at x = zero, P_x = atmospheric pressure at x metres height. The oxygen content in vol % is regarded constant to an altitude of 80 km (Chamberlain, 1978). The amount of air mass present at 50 and 80 km is 99.0 and 99.99 %, respectively of the total atmospheric mass.

The weight of the column of air on 1 cm^2 is on average 1.00 kg, which gives 10^7 g air/m^2. The volume percentage of O_2 is 20.946 ± 0.006 vol % (*see* also Tab. 1, which gives ± 0.002 vol %), which value is considered to be valid for the atmosphere to an altitude of 80 km due to vertical mixing processes (Chamberlain, 1978). The vol/vol percentage represents an equal mol/mol distribution, which gives for oxygen a value of 20.946 O_2 vol % (molecular weight 32), for nitrogen 78.1 N_2 vol % (molecular weight 28) and for argon 0.9 Ar vol % (atomic weight 40), reflecting 99.95 % of all air gases (Tab. 1). A mol and weight ratio of O_2/total air of 23.168 % can subsequently be calculated. For an atmospheric pressure of 10^7 g air/m^2 this results in: 2.32×10^6 g or 7.25×10^4 mol of O_2/m^2.

The O_2 content at the earth's surface can also be calculated from the formulas given in Figure 2, using the rule that 1 mol dry gas (1 Bar, 0 °C) is 22.4×10^{-3} m^3, which gives for 20.946 vol % of O_2: 9.35 mol O_2/m^3 at sea level. This results in: $O_{cum} = 6.91 \times 10^4$ mol O_2/m^2. For the total earth surface (*see* Tab. 2), the atmosphere contains: 3.53×10^{19} mol O_2, a value close to that of Budyko *et al.* (1987) of 3.75×10^{19} mol (1.2×10^{21} g).

Table 1

Composition of the lower atmosphere and exosphere (Encyclopedia Britannica, 1962; Chamberlain, 1978; Budyko et al., *1987; Veldkamp, 1965).*

CONSTITUENTS ATMOSPHERE	Formula	Volume %	Total mol x 10^{20}	Total g x 10^{21}
Nitrogen	N_2	78.084 ± 0.004	1.39	3.9
Oxygen	O_2	20.946 ± 0.002	0.37	1.2
Argon	Ar	0.934 ± 0/001	0.017	0.066
Carbon dioxide	CO_2	0.033 ± 0.001 (*)	0.0006	0.0026
Neon	Ne	18.18×10^{-4}		
Helium	He	5.24×10^{-4}		
Krypton	Kr	1.14×10^{-4}		
Xenon	Xe	0.087×10^{-4}		
Hydrogen	H_2	0.5×10^{-4}		
Methane	CH_4	2.0×10^{-4}		
Nitrous oxide	N_2O	0.27×10^{-4}		
Water vapour	H_2O		0.067	0.12

CONSTITUENTS EXOSPHERE Height km	N_2 No. atoms or molecules/cm^3	O_2 (**)	O	He	H	Average Mol. or At. weight
500	10^7	10^6	10^8	10^6	10^3	18
	(2.6×10^5)	(4.6×10^3)	(1.8×10^7)	(3.2×10^6)	(8×10^4)	(14.33)
750	(2.7×10^2)	(1.8)	(3.7×10^5)	(1.2×10^6)	(6.2×10^4)	(6.58)
800	10^5	10^4	10^7	10^5	10^3	16
1000	10^4	10^2	10^6	10^5	10^3	14
	(0.46)	(1.3×10^{-3})	(9.6×10^3)	(4.9×10^5)	(5.4×10^4)	3.94)
1500	10	0	10^4	10^5	10^3	6
2000	0	0	10^3	10^4	10^3	5

(*) Global average of 1980, with 2 to 3 % increase/decade due to fossil fuel burning.
(**) Data from Veldkamp (1965), in brackets from Chamberlain (1978).

This amount of oxygen is 99.0 % present in a layer of 50 km above the earth's surface, as can be calculated with the formulas in Figure 2. The atmosphere up to 80 km altitude contains 99.99 % of all air (and oxygen).

Carbon dioxide

The mass of CO_2 in the atmosphere for 1965 (Tab. 2) is 5.3×10^{16} mol CO_2. To this mass only a negligible amount is annually supplied by CO_2 emissions from volcanos, which is estimated at 3-4 $\times 10^{12}$ mol CO_2/yr, enough to replace the total amount of atmospheric CO_2 in 10^4 yr (Gerlach, 1991; *cf.* also Le Cloarec and Marty, 1991). The atmospheric mol O_2/mol CO_2 ratio is about 700, which is equal to the vol % ratio between O_2 and CO_2.

OCEANS

Oxygen

The average O_2 content of the oceans is approximately 5 l O_2/m^3 (at atmospheric pressure). This results in: (5 l/22.4 l) mol/m^3 = 0.22 mol O_2/m^3 sea water. For the total world ocean (Tab. 2), the oxygen reserve is then: 3.1×10^{17} mol O_2. Almost 120 times more O_2 is present in the atmosphere than in the oceans (Tab. 2).

Carbon dioxide

The amount of $\Sigma CO_2 = CO_2 + HCO_3^- + CO_3^{--}$ in the oceans (Tab. 2) is for the complete world ocean 2.9×10^{18} mol CO_2, which is a factor 55 times higher than the CO_2 in the atmosphere. The data taken here are from Bolin *et al.* (1979), fitting also with our own calculations based on the CO_2 tables made by Buch *et al.* (1932). The molecular ratio of O_2 over CO_2 in the oceans is 0.10.

OCEAN-ATMOSPHERE ANNUAL BUDGETS

Carbon-dioxide and temperature

Exchanges between oceans and atmosphere of the gases carbon dioxide and oxygen are the subject of many intensive and detailed studies. These exchanges are regulated by a number of synergetically working parameters related to: temperature; partial pressures in the atmosphere and in the

	ATMOSPHERE		OCEANS		ATMOSPH. + OCEANS	
	Earth surface: 5.1×10^{14} m^2 Continent surface: 1.5×10^{14} m^2		Ocean surface: 3.6×10^{14} m^2 Ocean volume: 1.37×10^{18} m^3 Av. Ocean depth: 3.8×10^3 m		(Total)	
	O_2	CO_2-C (1965)	O_2	CO_2-C	O_2	CO_2-C
Total mass in mol	3.75×10^{19}	5.3×10^{16}	3.1×10^{17}	2.9×10^{18}	3.781×10^{19}	2.953×10^{18}
Total mass in g	1.2×10^{21}	6.4×10^{17}	9.8×10^{18}	3.5×10^{19}	1.21×10^{21}	3.564×10^{19}
mol/m^2	7.35×10^4	1.04×10^2	8.6×10^2	8.1×10^3		
g/m^2	2.3×10^6	1.25×10^3	2.8×10^4	9.7×10^4		
mol/m^3 (at 1 atm.)	9.35	1.34×10^{-2}	2.3×10^{-1}	2.1		
g/m^3 (at 1 atm.)	299	0.161	7.4	25.0		

Atmosphere: total mol O_2/total mol CO_2 = 700
Oceans: total mol O_2/total mol CO_2 = 0.10 = 1/10
Total mol O_2 atm./total mol O_2 oceans = 120
Total mol CO_2 atm./total mol CO_2 oceans = 1.8×10^{-2} or 1/55

Average terrestrial prim. prod.: 12 mol Org-C/m^2/yr = 12 mol O_2/m^2/yr
Total terrestrial prim. prod.: 1.836×10^{15} mol Org.-C/yr = 1.836×10^{15} mol O_2/yr
Average oceanic prim. prod.: 6 mol Org.-C/m^2/yr = 6 or 6.9 mol O_2/m^2/yr (*)
Total oceanic prim. prod.: 2.16×10^{15} mol Org.-C/yr = 2.16×10^{15} or 2.48×10^{15} mol O_2/yr (*)
Total earth prim. prod.: (4.0-4.3) x 10^{15} mol Org.-C/yr = (4.0-4.3)x10^{15} mol O_2/yr

This leads to a mean turnover time for (atmospheric plus oceanic) oxygen of 8800-9450 yr (compare 2000 yr: Hall and Rao, 1987; 6000 yr: Holland, 1978), and a mean turnover time for (atmospheric and oceanic) carbon dioxide of 690-740 yr.

Table 2

O_2 and CO_2 data for atmosphere and oceans. For the latter, only the mean data are given. O_2 data: from this paper, Broecker (1970) and Budyko et al. *(1987); CO_2: using the tables of Buch* et al. *(1932) and from Bolin* et al. *(1979). Productivity data from Broecker (1970) and some from Berger* et al. *(1989) (*). Earth data from Bowden (1965).*

ocean surface waters; ocean-atmosphere interface exchange coefficients; atmosphere circulation patterns; wind at the ocean-atmosphere interface; ocean circulation patterns; biomass and its primary production; respiration; burial of organic matter and $CaCO_3$; pH with respect to ΣCO_2 solubility; and, finally, the time required to attain an apparent ocean-atmosphere steady-state partitioning.

There exists at present an impressive amount of data, obtained by the Joint Global Ocean Flux (JGOFS) and related Global Change studies, on the uptake of fossil fuel-derived CO_2 in the oceans, its distribution between atmosphere and ocean, and on the effect of the remaining atmospheric CO_2 on the "greenhouse" warming of the atmosphere.

Regarding the best data on historical CO_2 records of Antarctic ice cores, it is noteworthy that the atmospheric CO_2 level in the era from 160,000 years ago until the present, which has ranged between 200 and 300 ppmv CO_2, has been found to be linearly proportional to the change in global atmospheric temperature (δT in Fig. 3, line I). The increase of 0.09 °C/ppmv CO_2 is, however, not to be extrapolated to future temperature increases since the present atmospheric CO_2 rise is caused by additional CO_2 to the global atmospheric and ocean. Supposing that by the year 2 100 the level may rise to 1 500 ppmv (Anonymous, 1991), at 1 000 ppmv would have already a value of + 66 °C. The only reliable explanation for line I in Figure 3 is that it represents an apparent solubility curve of atmospheric CO_2 in the oceans for different temperatures (*see* also Fig. 16).

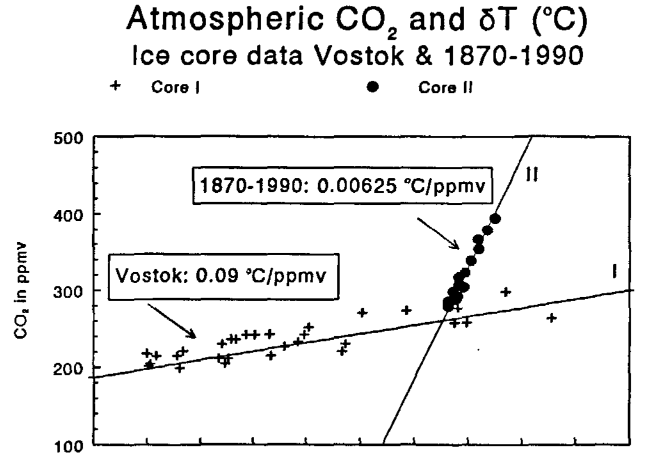


Figure 3

CO_2 atmospheric concentrations during the last climatic cycle as measured in Antarctic ice cores and correlated to the change in global atmospheric temperature δT. Solid line I: representing the apparent proportional correlation between atmospheric ppmv CO_2 concentrations and δT obtained from the Vostok ice core, representing a time scale reaching back 160,000 yr ago. Solid line II: the actual correlation as obtained from data of a recent ice core (1870-1990). For a present-day δCO_2/yr of 2 ppmv the rise of temperature is 0.0125 °C/yr. Data taken from Lorius et al. *(1990) for the Vostok ice core, and from Anonymous (1991) for the recent ice core CO_2 and δT data. The δT data are compared with those given by Coughlan* et al. *(1991).*

This problem of proportional correlation between atmospheric CO_2 and δT naturally also concerns the extrapolation of climatic sensitivity from paleoclimate reconstructions, except when burial or weathering of carbon is taken into account in the total pool of atmospheric and oceanic CO_2. Equilibrium between atmosphere and oceans should be attained. Although they fail to mention whether they included burial or weathering in the total pool of atmospheric and oceanic carbon, Hoffert and Covey (1992) arrive at a δT2x of 2.3 ± 0.9 °C, where δT2x stands for the temperature increase for carbon dioxide doubling.

Predicted future global temperature heating ranges between 2° and 5°C for an increase of heating with 4 $W.m^{-2}$ towards the year 2030, and taking into account the present average solar radiation of 340 $W.m^{-2}$ (Lorius, 1991). Since the end of the 18th century, when the addition of fossil fuel-derived CO_2 to existing atmospheric and oceanic CO_2 began, this heating was found to be less; ranging between 0.3 ° and 0.6 °C for an increase of 2.5 $W.m^{-2}$ solar heating. The contribution of atmospheric CO_2 to this greenhouse effect has been estimated at 61 % for 1990, the other contributing gases including CH_4 and N_2O (Tab. 3 A). A more realistic correlation for the present temperature increase is found from the CO_2 data of a recent ice core and an average known δT (land and sea), both representing a period between 1870 and 1990 (Anonymous, 1991). This correlation shows an increase of 160 ppmv CO_2/°C (Fig. 3: line II), or 0.00625°C/1 ppmv CO_2, which gives for the actual increase of 2 ppmv CO_2/yr an annual temperature rise of 0.0125 °C/yr. Here we have a correlation which is caused by the actual increase of the atmospheric CO_2 pool which is not yet fully partitioned between atmosphere and oceans, as it should be on the basis of the CO_2 solubility in the oceans. An additional point is that δT values of ice cores stand for temperature changes for high latitudes only. Temperature changes in glacial-interglacial periods were less at the equator than at high latitudes (Berner, personal communication).

The fossil fuel-derived CO_2 (Quay *et al.*, 1992), which is released at a rate of about 4.25 x 10^{14} mol CO_2/yr, will not rapidly equilibrate with the ΣCO_2 in the oceans. The turnover time of water masses, which transport CO_2 into the deep sea in polar regions, where the CO_2 is released at lower latitudes, is of the order of a thousand years (650 year in the Atlantic to 2000 in the Pacific according to Groen (1974)). Hence a disequilibrium between atmospheric and oceanic CO_2 will exist for several millennia after all fossil-fuel reserves have been exhausted.

The dissolution process of CO_2 into the ocean basin will affect the CO_2 equilibrium in sea water and the pH by shifting the equilibria given in the reactions (5) [Buch *et al.*, 1932; Wollast and Vanderborght, 1994].

$$CO_2 + H_2O \Leftrightarrow H^+ + HCO_3^- \ (K_1)$$
$$HCO_3^- \Leftrightarrow 2H^+ + CO_3^{2-} \ (K_2) \qquad (5)$$

Increased CO_2 concentration slightly raises the acidity (pH decrease) of sea water. The real correlation at dynamic equilibrium between atmospheric CO_2 and ΣCO_2 in the oceans can probably be modelled for a fictive

Table 3 A and B

A: PGH (= potential global heating) of gases, relative to carbon dioxide for a period of 100 years (Anonymous, 1991) and B: annual CO_2 production figures by fossil fuel burning and deforestation fires, and losses to the oceans.

A:

Greenhouse gasses	PGH	Emissions (1990, in 10^{12} g)	Relative contribution (in %)
CO_2	1	26000	61
CH_4	21	300	15
N_2O	290	6	4
CFC11	3500	0.3	2
CFC12	7300	0.4	7
HCFC22	1500	0.1	0.4
Others			10.6

B:

CO_2 emission to atmosphere	Methods + results 10^{15} g C/yr	Emission values 10^{14} mol CO_2/yr	References
I	F. Fuel: 5.37 Fires etc.: 1.21	4.475 1.01	Wollast and Mackenzie (1989)
II	IPCC evaluation F. Fuel: 5.4 ± 0.5 Deforestation: 1,6 ± 1.0	 4.5 ± 0.4 1.3 ± 0.8	Houghton *et al.* (1990)
III	F.Fuel: 5.3 Deforestation: 0.0-3.2	4.4 0-2.7	Tans *et al.* (1990)
IV	Emission, Table 3A: 7.1 (26000 × 10^{12} g CO_2)	5.9	Anon. (1991)
V	F.Fuel, 1989: 5.82 ± 0.38	4.85 ± 0.32	Marland and Boden (1991), cited by Keeling and Shertz (1992)
VI	F.Fuel 1970-1990: 5.1	4.25	Quay *et al.* (1992)
VII	Global emission: 6.5-7.5	5.4-6.25	Bouwman *et al.* (1992)
VIII	Oxygen depletion rate: 8.0 ± 2.0	6.7 ± 1.7	Keeling and Shertz (1992)

CO_2 loss from Atm. to Oceans	Method + results 10^{15} g C/yr	Transfer values 10^{14} mol CO_2/yr	References
I	pCO_2 gradients: 0.89	0.74	Broecker *et al.* (1986) cited by Merlivat *et al.* (1991)
II	pCO_2 gradients: 1.39	1.16	Maier-Reimer and Hasselman (1987) cited by Merlivat *et al.* (1991)
III	CO_2 Exch. coeff. atm.-ocean & satellite determinations: 1.17	0.975	Etcheto and Merlivat (1988)
IV	IPCC: 1.8 ± 1.4	1.5 ± 1.2	Houghton *et al.* (1990) cited by Sarmiento and Sundquist (1992)
V	2.0-4.7	1.7-3.9	Tans *et al.* (1990) cited by Sarmiento and Sundquist (1992)
VI	$\delta^{13}C$ method: 2.1	1.75	Quay *et al.* (1992)
VII	Tracer calibrated: 1.7-2.8	1.4-2.3	Sarmiento and Sundquist (1992)

average ocean temperature, taking into account the increase of total (atmosphere + oceans) CO_2 and the effect of temperature on the two equilibrium constants K_1 and K_2 of the reaction (5). The correlation given in Figure 3 (line I) should be used as a basis for the "pre-fossil fuel" correlation to which is added an increase of the total (ocean and atmosphere) amount of (fossil fuel-derived) CO_2. How this should be calculated is a matter of specialists in this field and is not treated in this overview. For the present oceans the pH is ranging from 7.9 to 8.4 (Skirrow, 1965).

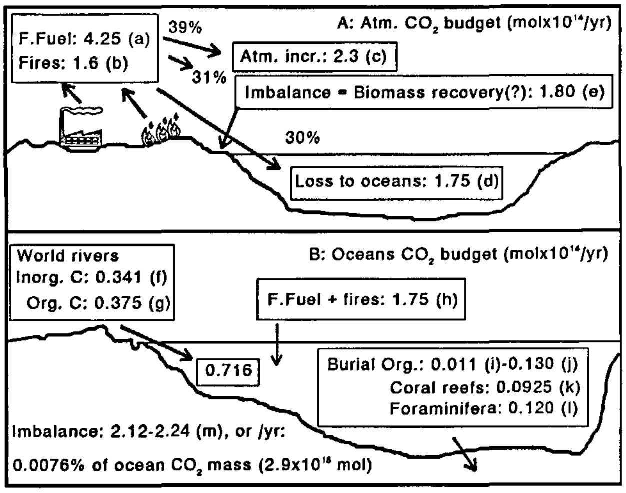
For CO_2, the exchange coefficient and net CO_2 fluxes from and to the oceans are determined worldwide by Etcheto and Merlivat (1988) and Merlivat *et al.* (1991) using SEASAT satellite scatterometer data. CO_2 is absorbed by the oceans in the cold polar waters and released to the atmosphere in the tropics. The net CO_2 flux into the oceans is determined at 0.975×10^{14} mol CO_2/yr (Etcheto and Merlivat, 1988), while other literature data range from 0.74×10^{14} mol CO_2/yr (cited by Merlivat *et al.*, 1991) to 1.75×10^{14} mol CO_2/yr [Quay *et al.*, 1992 (Fig. 4 A and Tab. 3 B)]. These fluxes are considered to represent the fossil-fuel and biomass fire-derived CO_2 from atmosphere to oceans. Since annually 5.85×10^{14} mol C is released as CO_2, 30 % is absorbed by the oceans, taking only the data of Quay *et al.* (1992), 39 % is accumulated in the atmosphere and 31 % may be recovered by regrowth of biomass. Since savannah fires are the major component of biomass fires (Artaxo *et al.*, 1993), this explains part of the imbalance due to recovery of vegetation growth of these savannahs.

A problem still unsolved concerns the present-day CO_2 fluxes between atmosphere and oceans. In Figure 4 B a budget is shown, in which the input of land runoff is fully taken into account. There exists an imbalance for the CO_2 exchange which is slightly higher (2.12-2.24 × 10^{14} mol CO_2/yr) than that detected by satellite scatterometer data (1.75×10^{14} mol CO_2/yr). The question is, however, whether a full exchange equilibrium should exist since, as we have seen, the time scale for arriving at an equilibrium between gases exchanged between atmosphere and oceans is in the order of several hundreds of years. A disequilibrium is, furthermore, possible because the imbalance amounts to only 0.0076 % of the total CO_2 mass of the oceans (Fig. 4 B).

Another interesting point is the burial of 0.22-0.34 × 10^{14} mol "CO_2"/yr as organic matter (0.011-0.13 × 10^{14} mol/yr), coral reef formation (1990 value, 0.0925×10^{14} mol/yr) and net sedimentation of foraminifers of 0.12×10^{14} mol/yr, taking into account the fact that foraminifers re-dissolve below the compensation depth. The suggestion of Ware *et al.* (1991) that coral reefs are sources of atmospheric CO_2 instead of sinks is locally correct, but misleading where the understanding of global processes is concerned. They demonstrate that during calcification, the water above reefs becomes more acid due to the removal of bicarbonate ions from the water, causing a corresponding change in pH which lowers the solubility of CO_2. Thus CO_2 is released to the atmosphere. However in respect to the world mass of atmospheric CO_2 and oceanic ΣCO_2 (= CO2 + HCO_3^- + $CO_3^{=}$) together, coral reefs can only be regarded as sinks, since from the total pool of CO_2, "CO_2" is removed. The same fact is also valid for other calcifiers like shelfish and foraminifera.

The net influx of fossil-fuel and biomass fire-derived CO_2 from atmosphere to oceans of 1.75×10^{14} mol/yr is a factor 2 1/2 times higher than that of the river-derived CO_2. Since the atmosphere to oceans CO_2 influx data derive from two different methods, namely $^{13}C/^{12}C$ evidence and satellite determination of the CO_2 air-sea exchange coefficient over the complete oceans, the budget calculation of Figure 4B still has some defects, at least for the ocean margins. These may be related to CO_2 degassing from coastal waters or burial of carbonates in coastal sediments, which escape $^{13}C/^{12}C$ and satellite measurements. This shows that the air-sea processes occurring in the continental margins cannot be neglected, and may have worldwide impacts on global change processes. Also Sundquist (1993) calls attention to this uncertainty in CO_2 budgets due to unidentified terrestrial CO_2 sinks.

Figure 4



A: CO_2 budget of atmosphere in mol x 10^{14}/yr. Data (see also Tab. 3B) from: a) Quay et al. *(1992): b) Houghton* et al. *(1990); c) Keeling and Shertz (1992); d) Quay* et al. *(1992). The budget results in an imbalance (e) of 1.80×10^{14} mol CO_2/yr, which can be partly explained by biomass recovery, in particular for savannah fires, which are the major contributors (Artaxo* et al., *1993).*
B: CO_2 exchange in mol 10^{14}/yr, between the atmosphere, rivers and the world oceans. Data (see also Tab. 2 and 3 B) are from (f) Sarmiento and Sundquist (1992), (g) for the load of organic matter from rivers, the same value is taken as given in Figure 14 h. The atmosphere-derived CO_2 entering the oceans is taken from Quay et al. *(1992), who give an average net annual oceanic CO_2 uptake of 1.75×10^{14} mol/yr of carbon for 4.25×10^{14} mol/yr of carbon released as CO_2 into the atmosphere by fossil-fuel burning, see also (a). Other authors (Etcheto and Merlivat, 1988) give a lower CO_2 (into the oceans) between 0.74 and 1.15×10^{14} mol CO_2/yr. The value of 1.75×10^{14} mol/yr is however in the range as summarized by Sarmiento and Sundquist (1992) who give a model estimate of 1.4-2.3 × 10^{14} mol/yr (i and j). The amounts of buried organic matter are also the same as those shown in Figure 14, the lowest given by Broecker (1970), the highest by Sarmiento and Sundquist (1992). (k) Coral reef formation is estimated (Kinsey and Hopley, 1991) at 0.0925×10^{14} mol/yr. (l) The net sedimentation of $CaCO_3$ by foraminifera, also taken for the complete oceans, is estimated at 0.120 x10^{14} mol/yr (Broecker and Peng, 1987). (m) The imbalance is 2.17×10^{14} mol/yr, which is only 0.0076 ± 0.0004 % of the total CO_2 mass in the oceans, being 2.9×10^{18} mol (Tab. 3 B).*

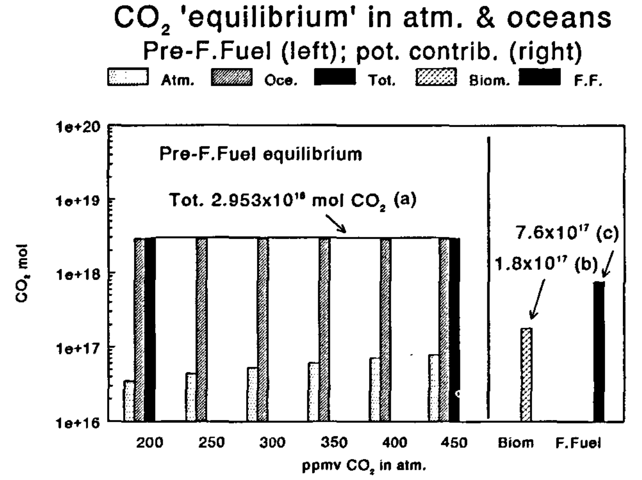


Figure 5

Left part: Pre-fossil fuel atmosphere-ocean distribution of CO_2. Bars representing: mol CO_2 in atmosphere (Atm.), oceans (Oce), calculated from 1965 values (Tab. 2) and in both together (Tot), regarded constant at 2.953 × 10^{18} mol CO_2 (a), for different ppmv CO_2 in the atmosphere. The atm./ocean CO_2 ratios range from 83.4 to 36.1 for 200 to 450 ppmv atmospheric CO_2. Right part: Potential CO_2 producers. Mass of mol CO_2 stored in biomass (Biom): 1.8 × 10^{17} mol CO_2 (b), from Keeling et al. *(1993). F. Fuel: 7.6 × 10^{17} mol CO_2 (c), also from Keeling* et al. *(1993).*

Given that 30 % of fossil-fuel and biomass fire derived CO_2 is absorbed by the oceans, the pre-fossil fuel equilibrium should be verified by estimating the possible contribution of each of the CO_2 atmospheric and ocean masses. These estimates are given in Figure 5 (left-hand part) for the mass of atmospheric CO_2 (Atm.), ocean-dissolved CO_2 (Oce) for a range of atmospheric concentrations between 200 and 500 ppmv, considering that the sum of atmosphere and ocean CO_2 masses is constant (2.953 x 10^{18} mol CO_2). From 200 to 500 ppmv, the absolute and relative amount in the oceans is rather constant, where the ratio of CO_2 mass in oceans and atmosphere decreases from 65.8 to 36.1. In the right-hand part of Figure 5, the equivalent amount of "CO_2" for biomass (Biom) and fossil-fuel carbon (F. Fuel) is given.

If the contribution of an increased world biomass (1.8 × 10^{17} mol CO_2; Fig. 5) were to be possible for an imaged increase of photosynthesis over respiration of either 0.1 or 1 %, this has as a result that 0.1 or 1 % of 1.8 × 10^{17} mol CO_2 (Fig. 5), which is 1.8 × 10^{14} or 1.8 × 10^{15} mol CO_2, is removed from the atmosphere and ocean CO_2 pool. Compared to the annual release of 4.25 × 10^{14} mol fossil-fuel CO_2 (Quay *et al.*, 1992), this means that the biosphere is certainly a potential accumulator of fossil-fuel CO_2. The condition, however, is that an increase of photosynthesis over respiration can only occur when more biomass and humus are permanently formed. On the other hand, current worldwide deforestation contributes 0.8-2.5 × 10^{14} mol CO_2/yr (Houghton *et al.*, 1991) to the atmosphere, which is rather the reverse of humus formation. A more precise figure for deforestation and biomass burning, offset by reforestation and biomass regrowth, of 0.52 × 10^{14} mol CO_2/yr is given by Bouwman *et al.* (1992).

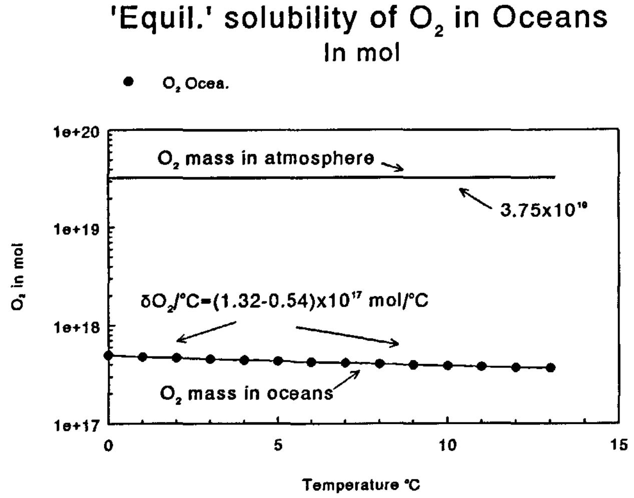


Figure 6

Potential saturation solubility of oxygen (in total mass) in the oceans as function of temperature (UNESCO, 1973), supposing the oceans to have a volume of 1.37 x 10^{18} m^3 (Tab. 2), a salinity of 35.0 and being homogeneous in temperature, and for 1 000 mBar atmospheric pressure. δO_2/°C = (1.32-0.54) x 10^{17} mol/°C.

For the ocean primary production/respiration system, an increased CO_2 uptake due to humus formation is less probable. When we compare (Fig. 4 B) the atmosphere-oceans CO_2 flux of 1.75 × 10^{14} mol CO_2/yr with that of the burial rate of organic carbon of 0.011-0.13 × 10^{14} mol "CO_2"/yr, we see that a 1 % change in photosynthesis over respiration should only cause a change in burial rate of organic matter of 0.00011-0.0013 × 10^{14} mol CO_2/yr, which is 0.006-0.07 % of the CO_2 air-ocean flux. It is therefore difficult to believe that even if the data used were not very accurate, the ocean primary/respiratory production system ("oceanic biological pump") would have any measurable effect on fossil-fuel carbon dioxide fluxes from atmosphere to the oceans.

OXYGEN AND TEMPERATURE

An increase of 1°C in the temperature of the oceans, due to a greenhouse effect, will affect oxygen solubility, and thus the atmosphere-ocean oxygen ratio. The solubility of oxygen for different temperatures in sea water of salinity 35.0 is given in Figure 6. It is essential to know not only that O_2 solubility decreases with higher temperature but also that δO_2 decreases from 1.32 × 10^{17} to 0.54 × 10^{17} mol O_2/°C between 0 and 13 °C. Compared to the total reserve of oxygen in atmosphere and ocean (3.75 × 10^{19} and 3.1 × 10^{17} mol, respectively), this will not be felt in the atmosphere, but can be of impact for the oceanic oxygen mass. Taking the actual annual temperature increase as given earlier at 0.0125 °C/yr (caption of Fig. 3), this results in an equivalent annual oxygen flux of the order of 1.65-0.675 × 10^{15} mol O_2/yr or 0.004-0.0018 % of the atmospheric oxygen mass and 0.5-0.2 % of the oceanic oxygen mass. This result has only hypothetical value for short time scales regarding the non-uniform temperature distribution in the oceans. But on the other hand it shows that the ocean oxygen budget is the most sensitive part of global heating, and that in the early Cretaceous period, with high temperatures, the ocean could indeed have become anoxic in certain regions (de Boer, 1986).

COMPARISON OF O_2 RESERVES WITH PRODUCTION AND UTILIZATION

Human needs

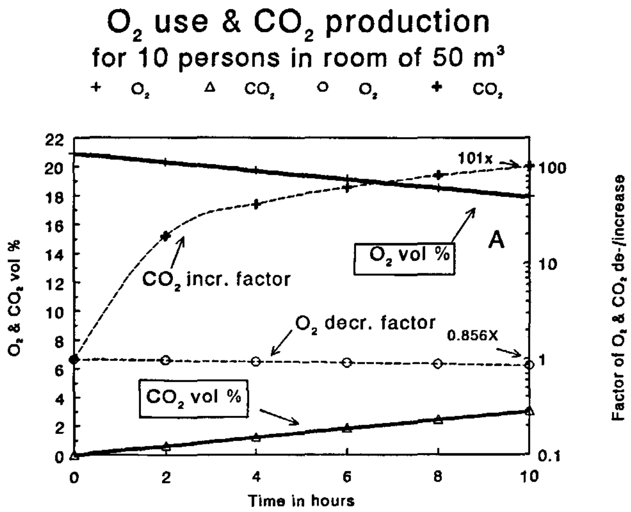
Human life is hardly ever jeopardized by lack of oxygen for respiration, except during mountain climbing to heights above 3 000 to 4 000 m. Although the content of oxygen in vol % is still 20.946, its concentration is reduced from 9.35 to 4.77 and 4.32 mol O_2/m^3, respectively (calculated from Fig. 2). After long exposure to these concentrations, the human respiratory system will show an adaptation by producing more red blood cells/ml blood, thus compensating for the reduced partial pressure of oxygen.

Even in an enclosed space of 50 m^3, such as the interior of a submersible, ten persons with an average oxygen use of 250 ml O_2/min per person will hardly feel a shortage of oxygen after ten hours, since O_2 will be still 0.856 of its original value (Fig. 7 A and 7 B). On the other hand, hypercapnia may occur due to elevated CO_2 levels (Fig. 7 C). After ten hours the CO_2 level has increased to 101 times its original value, resulting in a partial pressure of pCO_2 of 4 Torr (mm Hg). Although the human organism can tolerate for a short period a high pCO_2 in blood of 80 Torr, lower pCO_2 in the lungs of, *e. g.*, 45 Torr will result in severe hyperventilation, migraine and stomach problems [Le Péchon, 1993 (Fig. 7 C)].

Conurbations: Paris

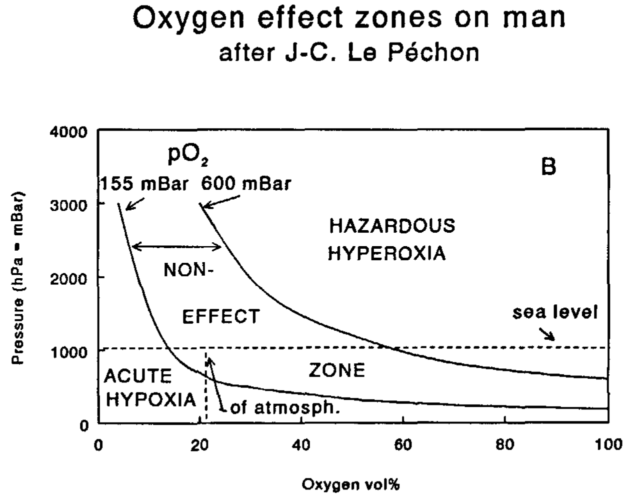
A similar calculation can be made for a large city, such as Paris. Supposing a complete absence of photosynthesis (and thus of oxygen production), the oxygen use for 10 million people, heating and cars is estimated at 225.9 mol O_2/m^2/yr, which equals the oxygen depletion of an air layer only 24 m in height (Fig. 8) during one year. Since the atmospheric circulation, even under calm weather conditions, is relatively large, there will be no shortage of atmospheric oxygen.

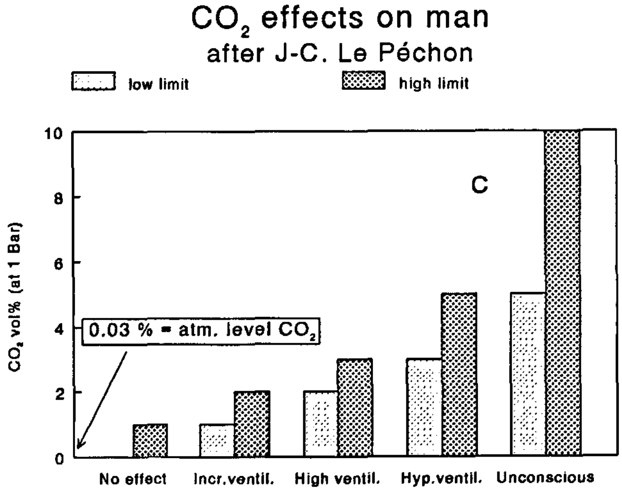
The danger is again the quantity of CO_2 produced. This is equivalent to an amount of CO_2 present in an equivalent atmospheric layer (all of 1000 mBar) of 16,850 m (Fig. 8). Hence at periods of high atmospheric stability and therefore low atmospheric circulation, CO_2 levels may rise to high levels, causing some of the nuisance effects mentioned above. The effects are however preceded by those caused by exhaust gases, like NOx, CO and smoke, which will play an overriding role.



Figures 7 A, B and C

A: Oxygen consumption in vol % in a space of 50 m^3 containing ten persons. Average human O_2 consumption is taken as 250 ml O_2/min/person or 15 l O_2/hr/person. Since 50 m^3 air contains 10,473 l O_2, this results in a decrease of 0.3 vol %/hr of O_2 for these ten persons. Consequently the CO_2 is rising with the same amount of 0.3 vol %/hr to 101 times its original value after ten hours. B: Oxygen effect zones on man, after Le Péchon (1993). See also Figure 1 B for evaluating the conditions during pre-historic time. C: CO_2 effects on man, after Le Péchon (1993). High ventilation is accompanied by absence of coordination, especially at exercise; hyperventilation leads to sweating and headache; unconsciousness is preceded by breathing problems, dizziness and may lead to stupor (coma).





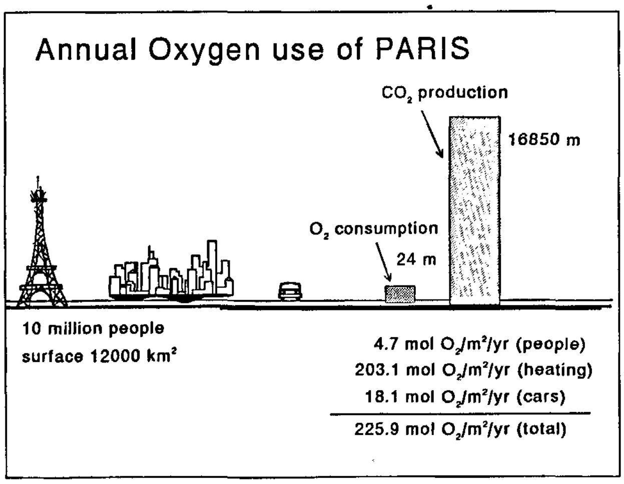


Figure 8

Oxygen use and CO_2 production of Paris, disregarding photosynthesis. Numbers expressed in mol $O_2/m^2/yr$. The columns reflect the metres layer of normal air (for all 1 000 mBar pressure), containing the consumed O_2 and produced CO_2.

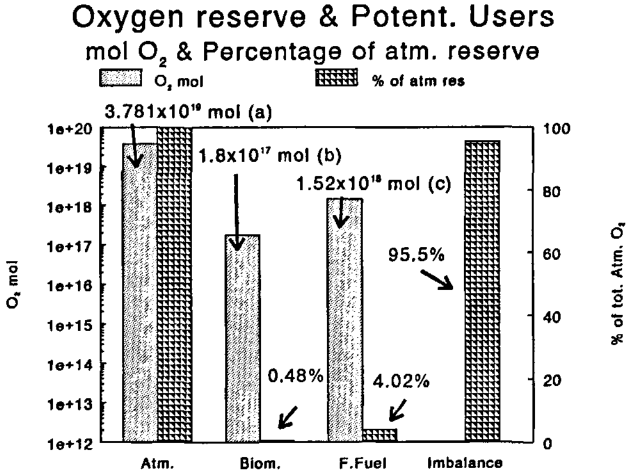


Figure 9

World atmospheric oxygen reserves (Atm.) (a), data see *Table 2. Known stocks of biomass + humus (Biom.) (b) and fossil fuels (F.Fuel) (c), expressed in mol oxygen equivalents (left bars) and % of world atmospheric oxygen mass (right bars. Note that % of total atmospheric oxygen reserve is used here and not vol %). The imbalance (95.5 %) is found by subtracting Biom and F.Fuel from Atm. Data (b) and (c) from Keeling* et al. *(1993).*

World major oxygen users

As estimated by Broecker (1970), four major existing and potential oxygen users can be distinguished. We added a fifth one: atmospheric chemical oxygen demand (COD). Two potential ones are given in Figure 9, expressed in total mass (mol O_2). The additional bars represent the percentage of these values with respect to he total atmospheric and oceanic oxygen reserve of 3.781×10^{19} mol O_2. The other users have too low an impact on a small time scale of a hundred years.

World respiration

The world respiration of flora and fauna is estimated to be in the range of $4.0\text{-}4.3 \times 10^{15}$ mol O_2/yr (Broecker, 1970; Berger *et al.*, 1989). Supposing respiration to be in equilibrium with the world production of oxygen by photosynthesis, this leads to a turnover time of 8 800-9 450 yr (Tab. 2) for both the atmosphere and oceans. Other turnover times are given by Hall and Rao (1987): 2 000 yr and Holland (1978): 6 000 yr.

Atmospheric chemical oxygen demand

Just as in the case of natural waters, we can speak of a chemical oxygen demand (COD) which is herewith defined as the annual oxygen consumption by reductive atmospheric compounds. Holland (1978) gives a COD value of 3.1×10^{12} mol O_2/yr for the volcanic gases consuming oxygen. So far, no reliable figures have been found for other oxygen-consuming atmospheric compounds (from CH_4, SO_2 to particulate carbon). Estimates by Artaxo *et al.* (1993) for POC emissions in smoke are equivalent to 5.8×10^{12} mol O_2/yr. Both "volcanic" and "smoke" COD amount together to 8.9×10^{12} mol O_2/yr, which is 2.4×10^{-5} % of the atmospheric oxygen reserve (ocean reserve not included). Thus the atmospheric COD can consume all atmospheric oxygen once every 6.5 million years. This result shows that atmospheric COD plays a minor role, even taking into account the inaccuracy of the data.

Burial of organic matter in the oceans

Burial of organic matter in the oceans (Fig. 3 B and 14) causes a residual production of oxygen (which is not consumed) of $0.011\text{-}0.13 \times 10^{14}$ mol O_2/yr. This amounts to $2.9\text{-}34 \times 10^{-6}$ % of the total (atmosphere + ocean) oxygen mass/yr.

Biomass and humus

The potential oxygen equivalent of the world biomass and terrestrial humus (Fig. 9) is estimated (Keeling *et al.*, 1993) to be equivalent to 1.8×10^{17} mol O_2 (or 0.48 % of the total oxygen mass). This figure has some consequences with respect to oxygen: 1) Since there exists a 1-to-1 conversion (and *vice versa*) of O_2 to CO_2 on a molecular and vol % basis [*see* formula (4, above)], O_2 fluctuations in the atmosphere are very limited and restricted by equal CO_2 vol % fluctuations over short time scales. Thus, even under microclimate conditions in the immediate vicinity of plant leaves in tropical forests, oxygen cannot increase more than 0.03 O_2 vol % relative to 20.946 O_2 vol %, since it has to counterbalance the available CO_2, which is at the level of 0.03 CO_2 vol %. Hence it is impossible that atmospheric oxygen can occur at levels higher than 20.976 O_2 vol %. This is an argument against the theories that forest fires should be triggered by (not really existing) elevated atmospheric oxygen concentrations. An increase by 0.03 O_2 vol % to at most 20.976 O_2 vol % is not significant enough, and the causes must be found elsewhere (dry seasons). On the other hand, there exists enough oxygen for fires to occur locally and temporarily reduce the O_2 level, but as we shall see below, this is negligible on a world atmosphere scale.

Fossil fuel

Burning of the total quantity of estimated reserves of fossil fuel would require an amount of 1.52×10^{18} mol O_2 (Keeling *et al.*, 1993), which is 4.02 % of the total atmospheric and ocean oxygen mass, taking into account that roughly two moles of O_2 are required for one fossil fuel carbon atom (Broecker, 1970). Whether this figure needs to be adjusted as far as the future is concerned is not essential, since the order of magnitude is evident. It becomes clear that even after a complete combustion of all world biomass (plants and forests) and fossil fuel reserves (0.48 + 4.02 % = 4.50 % of the total oxygen mass), the atmospheric oxygen would be reduced by at most 0.94 O_2 vol % and amount to 20.006 O_2 vol %. For the burning of fossil fuels only, this limit is 20.104 O_2 vol %.

Imbalance

Since the atmospheric oxygen has been produced due to burial of organic matter, we are faced in Figure 9 with a missing quantity of organic carbon to balance the 95.5 % excess of total atmospheric oxygen. This is even larger when paleo-oxygen, which is stored in sulphur and iron oxides, is taken into account.

The amount of buried organic carbon is estimated by Degens (1982) to be 3.1×10^{20} mol Org.-C, from which 3×10^{20} mol should be present in shales. In comparison and in accordance to Degens (1982) the world coal and oil reserves amount to only 5×10^{17} mol C and 1.7×10^{16} mol Org.-C, respectively. Supposing that each buried organic carbon atom requires 1-2 molecules of O_2, the oxygen equivalent is $3.1\text{-}6.2 \times 10^{20}$ mol O_2, which is a factor 8.2-16.4 times higher than the present atmospheric and oceanic oxygen reserve (= 3.781×10^{19} mol O_2). Budyko *et al.* (1987) confirmed this range of buried organic carbon as given by Degens (1982), to be equivalent to 3.68×10^{20} mol O_2 for continents, shelves, and ocean floors (Fig. 10), which is higher by a factor of 10 than the atmospheric oxygen mass.

The additionally stored oxygen in sulphur oxides can be found in oceanic $SO_4^{=}$ (concentration 2.7×10^3 g $SO_4^{=}/m^3$ containing 56.25 mol O_2/m^3), which contributes 0.78×10^{20} mol O_2. This represents an O_2 reserve twice that of the total atmospheric O_2 reserve. Forms like oceanic NO_3^- (2-5 g N/m^3 containing 0.22-0.54 mol O_2/m^3) are less significant in this respect. The remaining stored oxygen is to be found in sedimentary sulphur and metal oxides, in particular iron oxides. Budyko *et al.* (1987) presented a complete picture which is summarized in Figure 10. The part still lacking (imbalanced part of 1.92×10^{20} mol O_2) may be organic matter originating from the ocean and shelf bottom which has disappeared under the continents by subduction (personal communication of I. Foster Brown, Woods Hole Research Centre, USA, and Federal University Fluminense, Niterói, Brazil). The total sediment subduction is estimated at $(2\text{-}6) \times 10^{15}$ g/yr (Fyfe, 1992), which leads him to conclude that, given the mass of the continental crust of 1.6×10^{25} g, the process of full recycling occurs once every 3×10^9 years. This gives some support for the subduction hypothesis of the imbalanced organic matter. Since, however, Fe and S oxides are equally involved in subduction, further speculations cannot be permitted without the availability of a better set of data.

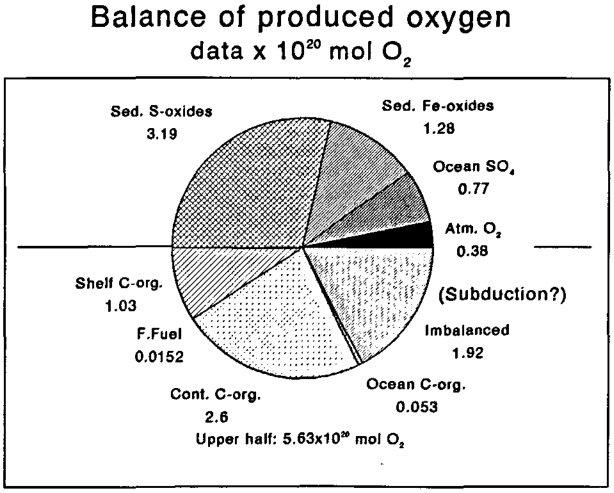


Figure 10

Pie chart of the balance of oxygen in the atmosphere and consumed in oxidizing processes over 1.8×10^9 years. Data, except for F. Fuel (Fig. 9), taken from Budyko et al. *(1987). It should be understood that the upper half of the figure concerns all net produced oxygen (difference between photosynthesis and respiration), while the lower part (expressed in oxygen equivalents) involves the fossil organic matter, including coal, thus produced. The imbalanced amount (1.92×10^{20} mol O_2) may be due to the difference between fossil carbon and oxidized sulphur and iron (in oxygen equivalents) in subducted ocean sediments beneath the continental plates (I. Foster Brown, Woods Hole Research Centre, USA, and Federal University Fluminense, Niterói, Brazil, personal communication), or due to inaccuracy of the data (see text). Calcium carbonate rocks and deposits, linked to the total global CO_2 reserve (formula 4 below), are not comprised in this figure.*

A recent estimate of Keeling *et al.* (1993) gives a much higher value for the sedimentary rock organic matter. Their value of $1{,}000{,}000 \times 10^{15}$ (10^{21}) mol of organic-C is far higher than that of Budyko *et al.* (1987) and as such twice the total atmospheric and "stored" oxygen of 5.63×10^{20} mol, given in Figure 10.

These results show that the given estimates require serious updating, in regard both to sedimentary organic matter, fossil fuel and charcoal, and to estimates on sedimentary sulphur-oxides and iron-oxides.

Present-day oxygen decreases

Fossil fuel burning will continue until all economically exploitable reserves have been exhausted. Oxygen is used for this process and atmospheric oxygen will decrease gradually, counter-correlated to the increase in CO_2 levels both in atmosphere and oceans.

The annual decrease due to this process will be at the level of the fourth decimal of the vol % as is the case with the increase of CO_2. This requires a very sensitive analytical technique, and only recently Keeling and Shertz (1992) have demonstrated that such an annual oxygen decrease indeed exists. At several places of the globe they measured the decrease accompanied by seasonal fluctuations (Fig. 11). These were, except for one region, countercorrelated to CO_2 fluctuations. The average decrease is of the order of 0.0004 O_2 vol %/yr.

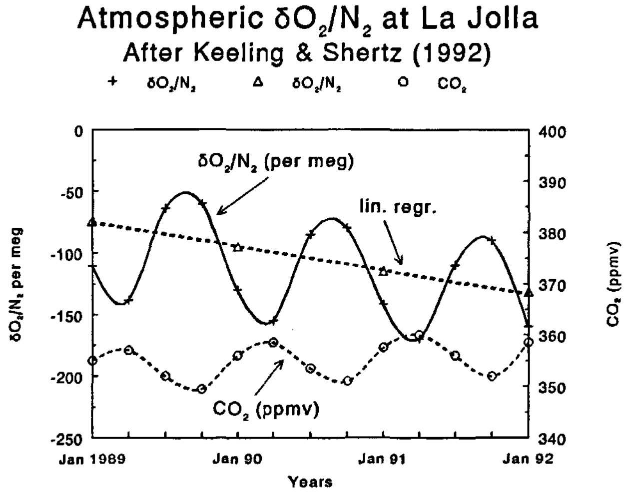


Figure 11

Actual decrease of atmospheric oxygen, as determined by Keeling and Shertz (1992) at La Jolla, USA, expressed in "per gem" units. The seasonal fluctuations anti-correlate with the CO_2 seasonal variations. The present annual O_2 change is given as $(6.7 \pm 1.7) \times 10^{14}$ mol O_2/yr, which is equivalent to about -0.0004 vol % O_2/yr. Data reproduced with the permission of Nature.

The earth as an open system with space

The earth has a surface area of 509.6×10^6 km^2. With regard to space the atmosphere is open, and losses of gaseous molecules are in principle possible. The atmosphere comprises a relatively thin gaseous layer around the earth (Fig. 12) to an altitude of about 100 km, consisting of the troposphere (0-20 km), the stratosphere (20-50 km) and the mesosphere (50-100 km). The ionosphere extends beyond 100 to about 1 000 km, whereas the exosphere extends from this distance into space up to the limit of action of the earth's magnetic field, which is between 10 to 20 times the earth's radius, or 60,000-120,000 km.

Gravitational and centrifugal forces, the earth's magnetic field and temperature determine whether gas molecules, atoms or ions will be retained by the atmosphere or be lost to space. The gravitation force F_g and centripetal acceleration force F_c are only in equilibrium at about 7 earth's radii, which is equivalent to a height of 50,000 km (Veldkamp, 1965). Since at this height in the exosphere ionization of gas atoms is practically 100 %, the magnetic earth field plays a role for retaining these ions in the magnetic field, whereas the high temperature between 900 and 1 100 °K (Yule, 1980; Flügge, 1984) causes very high speeds of the ions. Escape is probable above ionic velocities of 11 km/s, which can be attained and exceeded at these temperatures for the lighter ions, according to the formula (6), in which m is the atomic mass, T the temperature, k a constant and Cw the velocity.

$$C_w = \left(\frac{2kT}{m}\right)^{1/2}$$

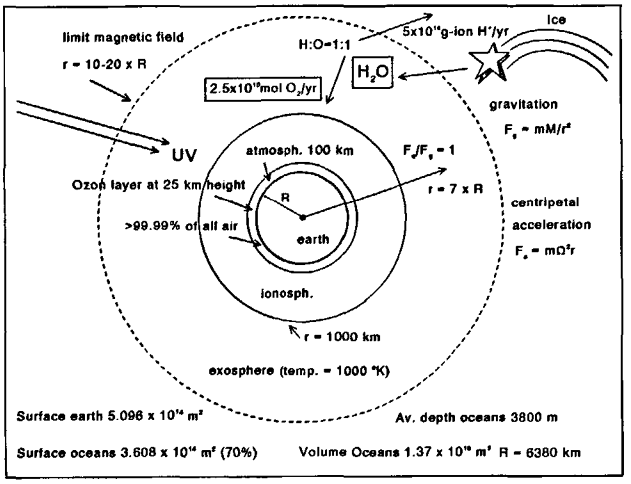


Figure 12

The atmosphere, composed of troposphere, stratosphere and mesosphere, is a relatively thin layer of 100 km height around the earth. In the enveloping ionosphere, reaching to a distance of 1 000 km, most molecules are dissociated into charged ions. The exosphere, limited by the range of the earth's magnetic field, has an open end to space. Loss of gas ions can occur when the centripetal acceleration force F_c becomes larger than the gravity force F_g, or $F_c/F_g >> 1$ (from $r >> 7 \times R$), in particular since ion velocities are large due to the high temperature. M = mass earth, m = mass gas ion, R is earth radius, r is distance from earth centre, Ω is earth rotation velocity (angular velocity).

As shown in Table 1, there are no more undissociated oxygen molecules present above 1 000 km height where the exosphere starts. At 2 000 km height the exosphere contains only O, He and H atoms. The fact that O and H are present and not N, should indicate a source for both H and O atoms. The ratio O/H is 1:1, which indicates that when the H^+ (or proton) is formed from dissociated H_2O, there should be at least twice the amount of H over O. Since the ratio is 10^3 O ions/cm^3: 10^3 H ions/cm^3 (Tab. 1) and given the uncertainty of the data, one may tentatively conclude only that part of the hydrogen (protons) has escaped to space. The consequence is an oxygen gain from dissociated water molecules. This dissociation may happen in the lower ionosphere with a transfer O and H ions to the higher ionosphere and exosphere. We may also imagine a gain through the dissociation of H_2O molecules, which molecules originate from space as ice crystals of comet debris (Frank *et al.*, 1986 *a* and *b*).

Estimates (Holland, 1978; Chamberlain, 1978; cf. also Schidlowski, 1980; Keeling *et al.*, 1993) place the escape of hydrogen close to 5×10^{10} g (or g-ions) H^+/yr. Since an equal number of H^+ and O^- ions is left behind, the gain of atmospheric oxygen is also 5×10^{10} g-ions of O^-/yr or 2.5×10^{10} mol O_2/yr. This is a factor 0.66×10^9 times less than the total atmospheric oxygen reserve. On an annual basis, these are insignificant quantities and the "space flux" may only have contributed about once in the course of the entire Neogäicum (= late Proterozoic + Phanerozoic, or from about 10^9 yr until now).

ENVIRONMENTAL EFFECTS ON PHOTOSYNTHESIS AND RESPIRATION

In order to understand processes that regulate oxygen production and consumption by the earth's flora and fauna, it is necessary to discuss some of the environmental external effects of light, temperature, CO_2, O_2 and nutrients that possibly control photosynthetic processes. But before doing so, we have to take it as axiomatic that there exists an amazing apparent equilibrium between global primary production and global respiration. Why such an equilibrium exists will not be discussed here, but an amazing fact it certainly is since, *e. g.*, fungi and bacteria (the largest contributors to respiration), which potentially can decompose any organic matter (also living material), do this only to a certain extent, thus allowing the existing apparent equilibrium to be maintained. Our problem is how a disequilibrium can occur and thus cause changes in atmospheric and oceanic oxygen. Photosynthesis is a coordinated serial oxidation-reduction process, involving a number of photochemical and enzymatic reactions (Berkaloff *et al.*, 1981; Larcher, 1983). The process starts with absorption of a photon, ends by incorporation of carbon and other inorganic elements into organic compounds, and takes place in a special organelle called chloroplast. Oxygen is liberated in the light-phase during which photons are captured, while electrons, coming from the oxidation of water, are transported to the electron acceptor, $NADP^+$ (Nicotine Adenine Dinucleotide Phosphate), which is reduced according to formula (7).

$$2NADP^+ + 2H_2O \rightarrow O_2 + 2NADPH + 2H^+ \qquad (7)$$

The products of this oxygen reduction are immediately utilized for the synthesis of organic matter, which is accompanied by: the reduction of CO_2 for the production of hexoses; the reduction of nitrates for the production of amino acids; and the reduction of sulphates for the synthesis of cysteine. These products also serve for the biosynthesis of fatty acids. The ratios between carbon fixation and other metabolic processes are not well established. In algae, reduction of nitrite to ammonium can also account for a photo-reduction at low irradiation (Curtis and Megard, 1987) and release of oxygen. The assimilation of CO_2 occurs along the so-called Calvin-Benson cycle or C_3 pathway (Larcher, 1983) in which the first-produced organic compound PGA (phosphoglyceric acid) contains three carbon atoms. The primary enzyme involved is Rubisco (ribulose-bi-PO_4 carboxylase/oxygenase), to which CO_2 and O_2 are competing for photosynthesis or photorespiration respectively. The cost of fixation of 1 CO_2 = 3 ATP + 2NADPH, in which ATP = adenosine Tri-Phosphate.

Several terrestrial plant species (*i. e.*, herbs, succulents and maize) have a primary and secondary CO_2 fixation cycle, the first occurring by the enzyme called PEPC (phosphoenol-pyruvate-carboxylase) which has a much higher affinity for CO_2 than Rubisco. The primary cycle is followed by a C_3 one in which the reduction to carbohydrate takes place. This is known as the Hatch-Slack-Kortschak cycle or C_4 pathway [first product is oxalo-acetic acid or OAA, containing four carbon atoms (Larcher, 1983)]. The cost of fixation for 1 CO_2 = 5 ATP + 2NADPH, which means 2 ATP higher than the Calvin-Benson cycle.

For our purpose it is the differences in the response of C_3 and C_4 plants to external conditions such as light, temperature, moisture, nitrate, CO_2 and O_2 changes that make them of major interest for potential atmospheric oxygen (and CO_2) regulation.

The various factors of interest may be summarized, using different and complementary literature, as follows:

Photosynthesis/photorespiration

C_3 plants can at the same time photosynthesize and photorespire (between 15 and 30 %). C_4 plants can only photosynthesize, while photorespiration is zero (Edwards and Walker, 1983)

Compensation concentrations

The CO_2 compensation concentrations are for C_4 plants (2 ppmv, sometimes given as up to 10 ppmv), much lower than for C_3 plants [50 ppmv, with a range of 30-70 ppmv (Black *et al.*, 1969; Goudriaan and Ajtay, 1979; Edwards and Walker, 1983; Larcher, 1983)].

Depression by O_2

Depression of photosynthesis by O_2 occurs only in C_3 plants, not in C_4 plants. This is due to the competition of O_2 and CO_2 for Rubisco which acts either as oxygenase or as carboxylase (Edwards and Walker, 1983).

Nutrients

An essential difference exists between the nutrient demand of C_3 and C_4 plants (Schmitt and Edwards, 1981). The latter plants have a lower nutrient demand for the same photosynthetic activity than the former. This is of high value for terrestrial regions and ocean surface waters with low fertilizer or nutrient concentration. On a global scale, the ratio of C_3 to C_4 species can potentially be influenced by the grip which man has on the world vegetation. At present the majority of terrestrial species are C_3 species, although the C_4 biomass of herbs in hot arid areas may override that of C_3 species (Hofstra and Stienstra, 1977; Werger and Ellis, 1981 and Fig. 13 B). Agriculture is focused on culture of economically valuable species, and C_4 plants (maize and sugar cane are examples of such C_4 plants) give a higher production per unit fertilizer.

Light curve

Light-dependency of photosynthesis has a maximum (saturation curve) for C_3 plants, not for C_4 plants (Ehleringer, 1978; Larcher, 1983; von Sengbush, 1989). Evidently

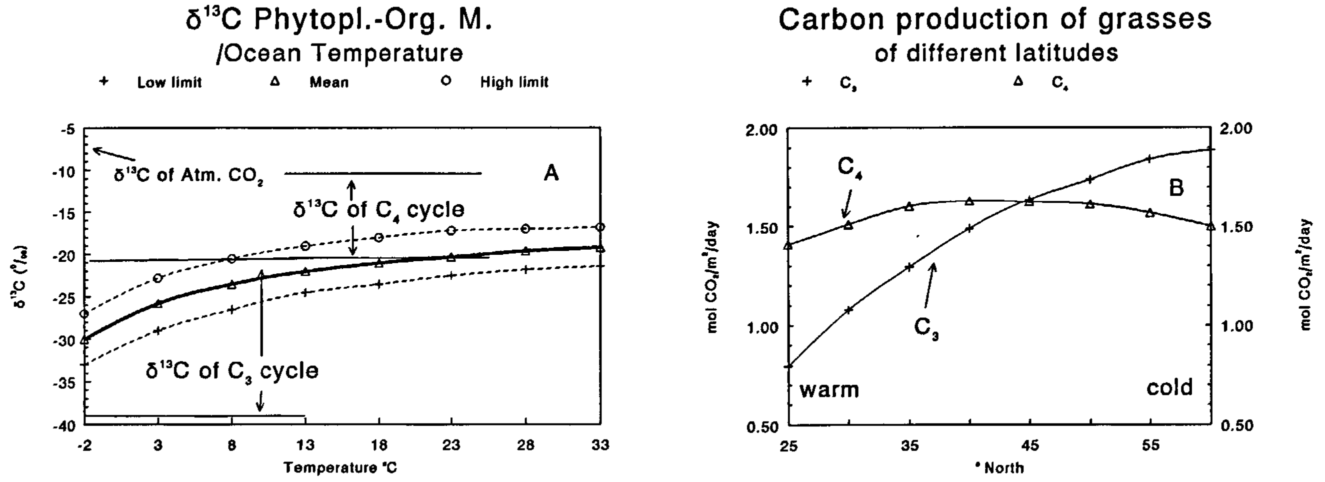


Figure 13 A and B

A.: $\delta^{13}C$ variations of ocean phytoplankton organic matter, collected by Descolas-Gros and Fontugne (1990). Range of $\delta^{13}C$ for C_3 and C_4 cycles are - 22 to - 34 ‰ and - 8 to - 16 ‰ respectively according to Descolas-Gros and Fontugne (1990), and - 20 to - 40 ‰ and - 10 to - 20 ‰ respectively according to Larcher (1983), the latter ranges are given in this figure. Permission to reproduce granted by the journals from which Descolas-Gros and Fontugne collected the data, namely Nature, Deep-Sea Research and Oceanologica Acta.

B.: C_3 and C_4 photosynthesis efficiency in mol $CO_2/m^2/d$ for terrestrial grasses of different latitudes of the northern hemisphere, after Ehleringer (1978). Data reproduced by permission of Springer-Verlag.

PEPC, even at the strongest light intensities, is capable of keeping pace with existing light irradiation.

Temperature

Temperature affects photosynthesis by way of enzymatic processes; the photochemical process is nearly independent of temperature, but enzymatic fixation of CO_2 increases with temperature, until a maximum value is reached. For a small range of temperature, the change of enzyme reaction rate is between 1.4x and 2.0x per 10 °C (Larcher, 1983). In general, C_4 plants can withstand higher temperatures than C_3 species, but there is genetically a large variation. Temperature has no effect on photosynthesis at low light intensities; however the photosynthetic rate will increase under intense light conditions for C_3 species, due to the sensitivity of Rubisco to temperature. High temperature favours photorespiration (in C_3 plants) by selective decrease of carbon dioxide relative to oxygen. In marine phytoplankton, Harrison and Platt (1980) and Côté and Platt (1983) have shown that 50 % of the photosynthesis variations were due to temperature changes. For land plants, high temperature may cause desiccation, to which C_4 plants are better protected than C_3 plants. Temperature also determines the distribution of C_4 plants and perhaps of phytoplankton (Fig. 13 A and B). C_4 land plants have a clear preference for higher temperatures, and will not be found in regions with frost (Werger and Ellis, 1981).

Distribution of C_3 and C_4 plants

The number of terrestrial C_4 species in northern Europe is small and clearly depends on the climate (Collins and Jones, 1985). From north to south the percentage of C_4 (in number of species) increases from zero in northern Europe to 4.4 % in the Azores.

C_4 algae

Although algae are not characterized as C_4 species (Badger, 1985; Descolas-Gros and Fontugne, 1990), a major number of algae contain a C_4-like photosynthetic pathway which deviates from C_3 ones in their CO_2 concentrating mechanism. This is linked to meeting the extra ATP requirements to concentrate CO_2, given the extremely low CO_2 level just outside the algae cell. Whether this occurs for all algae is not certain, but PEPC activities are measured in several species (Berkaloff *et al.*, 1981). When algal and cyanobacterial cells are depleted of CO_2, they switch to the uptake of CO_2 + HCO_3^- within themselves, using PEPC, in which case photorespiration is lost (Prof. P. Kuiper, Groningen, personal communication). The accumulation of inorganic C is accomplished by CO_2/HCO_3^- pumps, driven by light energy. Pumps are inactive at high CO_2. Descolas-Gros (1985) concludes that the involvement of PEP enzymes in marine phytoplankton species is relatively large and superior to that of typical C_3 "plants", such as Chlorella. Hence phytoplankton is possibly adapted to ocean systems in which HCO_3^- represents 90 % of ΣCO_2 (= CO_2 + HCO_3^- + $CO_3^=$) at a pH ranging from 7.8 to 8.2. The PEPC enzyme activity which is observed in various marine phytoplankton species may also change the ratio of "C_4"/C_3 photosynthesis in time during blooms (Descolas-Gros and Fontugne, 1990). Here "C_4" (also known as β-carboxylase) fixes HCO_3^-, while C_3 (through Rubisco) fixes only CO_2 (Beardall *et al.*, 1976; Geider and Osborne, 1992).

$\delta^{13}C$

There exists for both terrestrial and aquatic plants a difference in the carbon-isotope ratio in photosynthesis, which is between - 20 and 40 ‰ in C_3, and between - 10 and 20 ‰ in C_4 plants or algae (Larcher, 1983). $\delta^{13}C$ stands for:

$$\delta^{13}C = \left(\frac{^{13}C/^{12}C \text{ in sample}}{^{13}C/^{12}C \text{ in standard}} - 1\right) \times 1\,000 \qquad (8)$$

and is indicative for the C_3/C_4 plant ratio. The international standard is PDB (Peedee Formation, Cretaceous). Thus the $\delta^{13}C$ of vegetal organic matter can indicate the ratio of C_3 to C_4 photosynthesis. Indicative are, for example, the recent findings of $\delta^{13}C$ changes of soil humus for historical C_3/C_4 plant coverage ratio which changed from C_4 plants (dry area) to C_3 plants (present subtropical forest area) in the State of Paraná, Brazil (23°S, 53°W) in a period of less than 10,000 years (Pessenda *et al.*, 1993).

Photosynthetic efficiency/nutrient

A difference exists between C_4 and C_3 pathways concerning their photosynthetic efficiency as related to nitrogen nutrients. This efficiency is larger for C_4 than for C_3 plants. The C_4 plant maize has, *e. g.*, an efficiency of 6.7 mg CO_2/mg N/hr, while that of the C_3 plant rice is 5.9 mg CO_2/mg N/hr, determined both at 20°C (Schmitt and Edwards, 1981).

Terrestrial and aquatic feedbacks

Our evaluation of oxygen regulatory feedbacks on a short time scale in atmosphere and oceans has at each moment to take into consideration the fact that oxygen levels can only increase when photosynthesis is larger than respiration (C_3 plant photorespiration and animal and bacterial respiration), with burial of organic matter or increase of biomass as a result. We shall treat this for terrestrial and aquatic systems for the external factors (I) oxygen, (II) CO_2, (III) nutrients, (IV) temperature and (V) light, which are the major external factors that would be of impact for "short-term" oxygen regulation and burial of organic matter.

O_2

- Terrestrial

As mentioned earlier, atmospheric oxygen levels can change only slightly on a short time scale due to the fact that they are 1:1 anti-correlated to CO_2 in the order of 0.03 CO_2 vol %. No photosynthetic system will be sensitive enough to react to such a small deviation from 20.946 O_2 vol %. There will be no feedback based on atmospheric oxygen changes.

- Aquatic

In aquatic systems, O_2 can easily attain 200 % of the solubility saturation level during high primary production or decrease to zero when bacterial respiration is high. Hence O_2 can affect photosynthesis, and well for only C_3 photosynthesis, since C_3 can shift to photorespiration at high oxygen levels.

CO_2

- Terrestrial

Higher atmospheric CO_2 will cause greenhouse effects in the atmosphere and temperature rises (*see* further, temperature). High external atmospheric CO_2 concentration will increase photosynthesis both in C_4 and in C_3 plants. Some C_4 plants can close their stomata prior to an increase of photosynthesis in order to reduce loss of water, so the effect is (temporarily) lower than for C_3 plants. Low CO_2 reduces C_3 activity earlier than C_4 activity because of the difference of their compensation points: 50 ppmv CO_2 (0.005 CO_2 vol %) for the C_3 enzyme Rubisco and 2 ppmv CO_2 (0.0002 vol % CO_2) for the C_4 enzyme PEPC. For both C_3 and C_4 species, this productivity acts only as feedback for increasing or decreasing when it is accompanied by an increase or decrease, respectively of biomass and humus formation [*see* formula (4, above)], since otherwise production is balanced by respiration. The different reactivity of C_3 and C_4 plants has also been modelled for the biosphere of the next 0.1 to 1.5 Gyr (10^9 year), when it is expected that due to diminishing atmospheric CO_2 levels C_4 plants can survive for a much longer period than C_3 plants (Caldeira and Kasting, 1992).

- Aquatic

Increased atmospheric CO_2 will only slightly affect the CO_2 level in the oceans, since the latter contain 55 times more CO_2 than the atmosphere. Thus there will be no feedback based on increased atmospheric CO_2, or at most very little (< 2 % of effects on land).

Nutrients

- Terrestrial

Nutrient deficiencies will occur with strong biomass growth. This may act as a feedback to limit primary productivity, biomass and humus formation and consequently oxygen production.

- Aquatic

Nutrient deficiencies occur usually at times of high primary productivity in spring, summer and autumn. The corresponding high temperatures will at the same time stimulate surface layer stratifications and subsequently hamper nutrient fluxes from deeper layers to the surface euphotic zones where photosynthesis occurs. Nutrient availability during prehistoric warm climate periods was additionally influenced by sea-level rises, land erosion and changes in ocean circulation and upwelling, thus supplying the oceans with additional nutrients (Oppo and Fairbanks, 1990). Increased burial of organic carbon will cause a surplus of oxygen with respect to the usual production/respiration equilibrium. Thus nutrients play a role in the feedback

Temperature

- Terrestrial

Higher temperatures favour the presence of C_4 plants to the detriment of C_3 plants, as can be learned from the $\delta^{13}C$ values for phytoplankton (Fig. 13 A) and grasses (Fig. 13 B). This will affect C_3/C_4 species distribution in favour of the latter, and thus increase the total efficiency of photosynthesis/amount of nutrient. Since these higher temperatures are caused by greenhouse effects at elevated CO_2 levels, more CO_2, relative to nutrients, will be bound. This process acts as a feedback to reduce the greenhouse effect but may favour more biomass and humus formation and a resulting oxygen production.

- Aquatic

Higher temperatures of surface ocean waters will favour stratification (Oppo and Fairbanks, 1990), and thus reduce the exchange of nutrients between deeper and surface waters. On the other hand, burial of organic matter will be increased, thus causing an excess of photosynthesis over respiration. The net effect is an oxygen release to the atmosphere and an excess uptake of CO_2 by the oceans. This will have as result an increase in burial of organic matter (causing oxygen "over" production) but also act as a feedback to reduce greenhouse heating. Whether there is a change from C_3 to C_4 photosynthesis is not yet clear, although the different $\delta^{13}C$ values of phytoplankton in the oceans (Fig. 13 B) indicate a correlation with temperature (Beardall *et al.* 1976; Descolas-Gros and Fontugne, 1990).

Light

- Terrestrial

If gas exchange is not restricted by environmental factors such as water supply and temperature, net photosynthesis parallels light availability up to a saturation level for C_3 plants, while there are no restrictions for C_4 plant growth. Photo-inhibition in C_3 plants at excess irradiation usually occurs temporarily during midday, and is rarely irreversible. Variable cloud cover will have effects causing similar fluctuations in photosynthetic rates for both C_3 (below saturation level) and C_4 plants. High light conditions act as feedback for CO_2 reduction and oxygen supply, at least when there is humus formation

- Aquatic

Algal growth depends on light absorption in the water column, which usually results in a maximum photosynthetic activity at some distance below the water surface, above which there is photo-inhibition and below a photo-adaptation with depth decreasing radiation. Light thus has an impact on the photosynthetic processes and has the same feedback possibilities as on land.

GLOBAL "SHORT-TERM" FEEDBACK POSSIBILITIES

Considering all the effects of external factors on photosynthesis by C_4 and C_3 plants, and on photorespiration by C_3 plants and animal and bacterial respiration, we can only conclude that global short-term regulation of atmospheric oxygen is not different from that of long-term regulation. The difference should be the speed of humus formation (and its burial), or erosion, burning and decomposition of buried organic matter. In fact these are the same processes as burial and weathering which caused the long-term changes given in Figures 1 A and 1 B. Nevertheless, it is the living material that is at the basis of any change in atmospheric oxygen variation (except for fossil-fuel burning) and there may still exist a short-term regulation process superimposed on the long-term variations. The question is, how short can such a superimposed variation be? We will discuss this for four cases, to wit: 1) global time scales; 2) time scales for the oceans; 3) time scales for continental shelves; and 4) time scales for glacial to interglacial periods.

Global time scales

We have demonstrated that all free and bound oxygen on earth has been produced by living vegetal material, whose net production from 3.2 billion years ago until the present amounts to fifteen times the present atmospheric oxygen mass (Fig. 10). We have seen that each atmospheric oxygen mass passes on average once every nine thousand years through living material (Tab. 2). If photosynthesis were to fail hypothetically for a time span of 0.9 year (328 days) and total respiration were to remain constant, this would only change the atmospheric oxygen by a factor 1/10 000 times 20.946 vol %, which is 0.002 vol %. If, on the other hand, photosynthesis were to exceed total respiration by, for example, 1 %, causing an equivalent increase of biomass and buried humus, it would take 100 times the atmospheric oxygen turnover time or 900,000 years.

Time scales for oceans

The world oceans have, on the one hand, a relatively small oxygen content which is 1/120 (Tab. 2) of that of the atmospheric oxygen reserve. But on the other hand, the oceans have a very large interface with the atmosphere, amounting to 70 % of the earth's surface and a primary productivity which ranges from 30 to 300 g C/m^2/yr (Berger *et al.*, 1989). Despite the fact that the oceans only contain 0.22 % of the world's biomass, their primary productivity is in great measure due to a much more rapid turnover of the oceanic biomass, *viz.*, 54 % of the world primary production (*cf.* Tab. 2 and Taube, 1992). In principle, the ocean primary productivity is flexible enough to react on changes in O_2, caused by the imbalance of photosynthesis over respiration. Such an imbalance is thought to be controlled by varying nitrogen-nutrients over periods of 1,000 to 10,000 years (McElroy, 1983), reacting on changes in oceanic circulation and upwelling, sea-level rise, erosion and stratification. Since the exchange of oxygen between atmosphere and oceans is rapid enough, as we shall see later, the oceans can probably contribute substantially to the regulation of atmospheric oxygen, as was already mentioned (de Boer, 1986) due to higher burial of organic matter in warmer periods.

The question is, however, in which period of time can a measurable effect be observed? A calculation example will make it clear that for a supposed 0.1 vol % change of atmospheric oxygen, this is still a long period. A gain of 0.1 vol % of atmospheric O_2 would involve per square metre world ocean surface a flux of $(7.25 \times 10^4$ mol $O_2/m^2) \times (1/0.70) \times (0.1/20.946) = 494$ mol O_2/m^2. The average annual primary production of the world oceans of 30 gigatons carbon (2.5×10^{15} mol Org.-C/yr; Berger *et al.*, 1989) or 6.9 mol $O_2/m^2/yr$ is a factor 72 times lower than the above hypothetical gain 494 mol O_2/m^2. Supposing that compensation can occur through a 1 or 0.1 % ocean primary production increase over respiration (and subsequent burial of organic matter), the atmospheric adjustment will require 7,200 or 72,000 yr, respectively. In order to replace all 20.946 vol % O_2, this would take 1.5 x 10^6 or 1.5 x 10^7 years, respectively. Such a cycle could occur in the 1.8 billion years of photosynthetic oxygen formation 1,200 or 120 times, respectively. Although these numbers have only illustrative value, they show the range in which changes could be encountered.

It is necessary to consider the effect of increased photosynthesis over respiration on the burial rate of organic matter in the oceans. For the 1 and 0.1 % increase of the above given production of 6.9 mol $O_2/m^2/yr$ over respiration, this results in a burial increase of 0.069 or 0.0069 mol $O_2/m^2/yr$, respectively. For the world oceans, the actual average deposition rate of organic matter calculated from Figure 14, is 0.003-0.036 mol $O_2/m^2/yr$. Burial should therefore increase by a factor 2 300 or 230 %, respectively, for the lowest burial value and 190-19 %, respectively, for the highest value. This is difficult to imagine, unless parts of the oceans become anoxic below the euphotic surface layer.

A remaining question is whether the involved oxygen fluxes through the ocean surface could sustain such an oxygen flow from oceans to atmosphere. Oxygen fluxes through the sea/atmosphere surface have been determined (Liss and Merlivat, 1986; Stigebrandt, 1991) to occur at values higher than those given above. For the Bothnian Sea, Stigebrandt (1991) determined a net annual oxygen flux from atmosphere to the sea of 4.06 mol $O_2/m^2/yr$, which is substantially higher than the required fluxes of 0.069 or 0.0069 mol $O_2/m^2/yr$ for the taken 1 or 0.1 % increase of photosynthesis over respiration. Thus it can be concluded that the interface flux of O_2 will therefore not be a limiting factor for a possible regulatory process of atmospheric oxygen by oceanic oxygen.

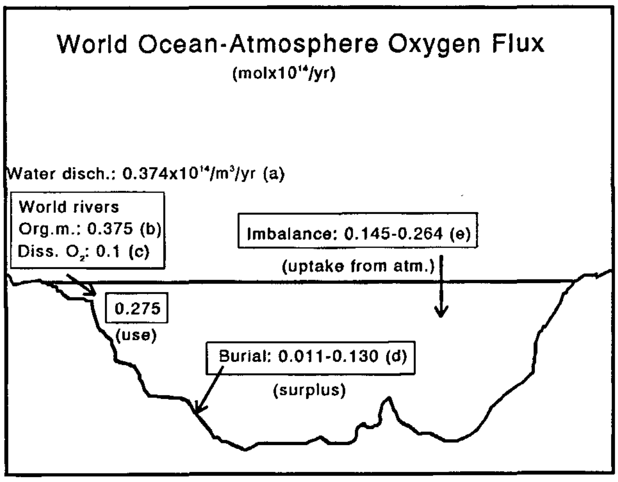


Figure 14

The world river input into the oceans is estimated at 0.374 x 10^{14} m^3 *water/yr (a) by Spitzy and Ittekkot (1991). These rivers contain about 400-500 million tons of organic matter-carbon (Spitzy and Ittekkot, 1991 for DOC + POC, and Meybeck, 1993 for total Org.-C), which is equivalent to an oxygen use (1:1 ratio 1 atom C to 1 molecule* O_2*) of 0.33-0.42 x* 10^{14} *mol* O_2*/yr; an average of 0.375 x* 10^{14} *mol* O_2*/yr is taken (b). Supposing the oxygen content of these rivers to be about 8 g* O_2/m^3*, this gives a river-oxygen flux of about 0.1 x* 10^{14} *mol* O_2*/yr (c). This results in a net oxygen use of 0.275 x* 10^{14} *mol* O_2*/yr, if averaged for the world oceans. The burial of organic matter (see also Fig.4) ranges from 0.011 x* 10^{14} *mol* CO_2*/yr (Broecker, 1970) to 0.130 x* 10^{14} *mol* CO_2*/yr (Sarmiento and Sundquist, 1992), which results in a oxygen surplus of the same molar value (d). The imbalance should be compensated at equilibrium by a net flux of 0.145-0.264 x 1014 mol* O_2*/yr from the atmosphere into the oceans.*

This does not mean that the oxygen regime in the oceans is insensitive to changes in the ratio of photosynthesis and respiration. An excess of photosynthesis may be enhanced by "new" production caused by anthropogenic nutrient releases into the oceans, or changes in upwelling patterns, either in continental margins or in open sea frontal regions, and where respiration is not increased to the same extent. We have already seen that the oxygen solubility (Fig. 6) is sensitive to global heating, which eventually may cause anoxicity, which strongly enhances burial of organic matter. For the Mediterranean Sea this is demonstrated by Béthoux (1989). A prediction is given that in both the Eastern and Western deep waters of the Mediterranean, due to a 3 % annual increase in nutrient discharges, anoxic conditions may occur in deep basins after the year 2050. Many studies in the JGOFS (Joint Global Ocean Fluxes Studies) programmes are concerned with this topic.

Time scales for continental shelves

As was already mentioned in the paragraph on air-sea exchange of CO_2 (*see* Fig. 4), continental shelf processes may have a non-negligible impact. For the oxygen exchange of the oceans, this seems equally the case (Fig. 14). The input of organic matter by rivers is estimated by Meybeck (1993) at 400 million ton of organic C/yr, which is equivalent to 0.33 x 10^{14} mol Org.-C. Another value is given by Sarmiento and Sunquist (1992) ranging between 0.25 and 0.42 x 10^{14} mol/yr. For an average of 0.375 x 10^{14} mol/yr, this will cause a potential oxygen use of the same value. The world rivers bring into the oceans an additional 0.1 x 10^{14} mol free-dissolved O_2 (Fig. 14). Burial of organic matter (Fig. 4) ranges from 0.011 to 0.13 x 10^{14} mol/yr, giving a surplus of oxygen to the oceans. The result of these inputs and outputs is that the oceans are deficient in oxygen, and in order to attain an atmosphere-ocean equilibrium, a flux of 0.145-0.264 x 10^{14} mol O_2/yr from atmosphere to oceans is required to counterbalance input and burial. In the case that global changes of atmospheric oxygen are to be compensated by oceanic oxygen, the effects of changing run-off from the continents will not be negligible, such as the changes in deposition of organic matter on the continental shelves. It is difficult to speculate here on time scales. As in the case of the CO_2 ocean margin budget mentioned earlier (Fig. 4), there are too many unknown factors.

Time scales for glacial to interglacial periods

It appears that the main factors influencing climate within a time frame of 10,000 to 100,000 years are the orbital periods of the earth. These so-called Milankovitch cycles

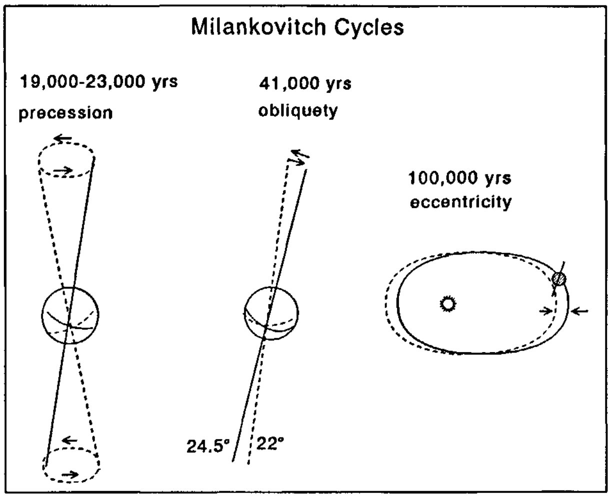


Figure 15

Milankovitch cycles of spinning (precession) of the earth's axis (19,000-23,000 yr), eccentricity of the axis (41,000 yr) and eccentricity of the earth's orbit (100,000 yr), after de Boer (1986).

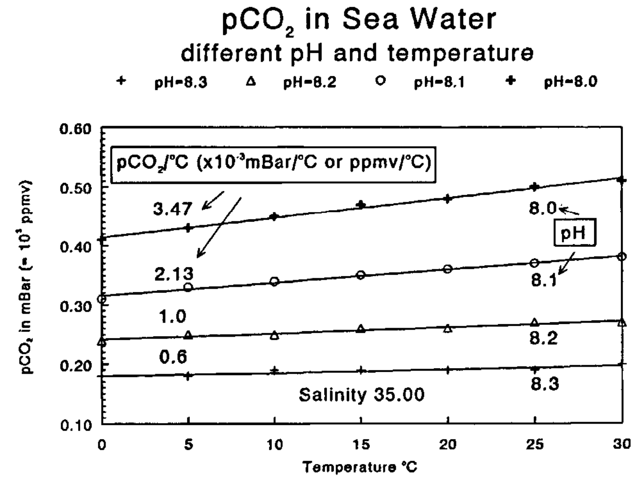


Figure 16

Solubility of CO_2 in sea water of 35 salinity and pH = 8.0 to 8.3 at different temperatures, given for pCO_2, taken from the classical tables of Buch et al. *(1932).*

(Fig. 15) are related to the periods in the precession of the earth's axis (21,000 years), the tilt angle or obliquity of the rotation axis of the earth (41,000 years), and the eccentricity of its orbit (100,000 years, Degens, 1989; de Boer, 1990/1991). The result is that the present average solar radiation, which is for 50° N at the level of 35,500 kJ/m^2/day, can fluctuate between 34,000 and 38,000 kJ/m^2/day. The range between maximum and minimum solar radiation is 10 % of the present-day radiation. The Milankovitch effect has been modelled by Berger *et al.* (1991; 1993), whose model is compared with six other models of varying complexity to predict the climate for the next 10,000 to 100,000 years. With respect to the present interglacial period, they calculated that the long-term cooling trend due to reduced insolation began some 6 kyr ago and will continue until a slight stabilization at 15 kyr after present (AP), with a cold interval centred at 25 kyr AP and a major glaciation at 55 kyr AP. These predictions have not so far taken account of anthropogenic disturbances. The real temperatures will also depend on the momentum of the global heat system, which plays a role distinct from such disturbances.

Concerning a "warming" momentum, the question is posed here whether the dissolution of CO_2 from the oceans will quantitatively add a stimulant to the greenhouse effect of the atmosphere and thus have an impact on atmospheric oxygen regulation. High CO_2 levels, causing greenhouse effects, are indeed present during interglacial periods, while during ice ages atmospheric CO_2 concentrations are low (Shackleton *et al.*, 1983). Barnola *et al.* (1987) have demonstrated this effect on the basis of careful measurements of the CO_2 concentrations of an Antarctic ice core (Fig. 3 line I). There are also chain reactions such as increased CH_4 atmospheric concentrations (Raynaud *et al.*, 1993) and increased DMS (dimethyl-sulphide) production by phytoplankton. CH_4 will stimulate greenhouse heating although its relative contribution is less (*see* Tab. 3 A) than that of CO_2. DMS in oxidized form gives rise to cloud nuclei and subsequent cloud formation in the atmosphere, which affects albedo and infrared reflection. Snow cover and water vapour in the atmosphere (Lorius *et al.*, 1990; Legrand *et al.*, 1991), will act as feedback and cause a temperature decline.

With an average increase of temperature of the oceans (Fig. 16) the solubility of total CO_2 (including HCO_3^- and CO_3^-) decreases and CO_2 is liberated from the oceans to the atmosphere. This results in an increase of 0.6 to 3.47 ppmv CO_2/°C for a pH range of 8.3 to 8.0, supposing equilibrium to be attained with atmospheric CO_2. Bearing in mind that the present δCO_2 is about 2 ppmv/yr, which is supposed to cause greenhouse effects over a time period measured in decennia, it is quite possible that the Milankovitch warming is auto-stimulated by the CO_2 from the oceans. As we have seen, oceanic water mass circulation involves turnover times of up to a thousand years. The CO_2 degassing due to temperature rise is at least of this order of magnitude. As already mentioned, the system of degassing is very complicated due to the ocean circulation patterns and the reaction of the climate patterns in which for example, those of the Gulf Stream play a role for the climate of Europe, and those of the South American El Niño for the South American climate frontal systems (Martin *et al.*, 1993).

Concerning oxygen changes during interglacial periods, time scales of many thousands of years would allow some changes in burial rates of organic matter. But the time scales of measurable oxygen changes will be of the same order of magnitude as discussed earlier, which means almost non-existent for interglacial periods.

FINAL CONCLUSION

Terrestrial and oceanic systems of photosynthesis and respiration of the earth's flora and fauna contain the necessary components for auto-regulation of atmospheric oxygen. The question as to how this occurs quantitatively requires many detailed and global studies, but we may conclude that the relatively stable oxygen content of the atmosphere is the result of a complex short-term and long-term period regulatory processes, which are primarily caused by the earth-sun constellation and resulting heat budget and cyclic world-climate changes, of which the glacial-interglacial cycles are the shortest. The feedback processes are able to maintain oxygen rather constant over periods of thousands of years, superimposed on a multimillennial cycle with extremes of oxygen between larger limits.

No evidence is found for an autoregulation of atmospheric oxygen solely based on changes in oxygen. Oxygen concentrations are therefore the consequence of larger terrestrial and aquatic loops in which factors of temperature, light, nutrients and CO_2 play a role; for longer periods, elements such as sulphur and iron are involved. Hence the present level of 20.946 vol % of atmospheric oxygen is merely temporary, and will change in the course of millions of years. The question of an optimum concentration for sustaining life on earth is equally time-dependent; but bearing in mind that these changes occur over periods of the order of millions of years, evolutionary processes are likely to keep pace with oxygen changes. It remains an amazing fact, however, that global photosynthesis so equally balances global respiration; no explanation of this is offered in the present overview, but it constitutes the keystone of the global stability of oxygen.

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