Review

Land plants equilibrate O_2 and CO_2 concentrations in the atmosphere

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Abstract

The role of land plants in establishing our present day atmosphere is analysed. Before the evolution of land plants, photosynthesis by marine and fresh water organisms was not intensive enough to deplete CO_2 from the atmosphere, the concentration of which was more than the order of magnitude higher than present. With the appearance of land plants, the exudation of organic acids by roots, following respiratory and photorespiratory metabolism, led to phosphate weathering from rocks thus increasing aquatic productivity. Weathering also replaced silicates by carbonates, thus decreasing the atmospheric CO_2 concentration. As a result of both intensive photosynthesis and weathering, CO_2 was depleted from the atmosphere down to low values approaching the compensation point of land plants. During the same time period, the atmospheric O_2 concentration increased to maximum levels about 300 million years ago (Permo-Carboniferous boundary), establishing an O_2/CO_2 ratio above 1000. At this point, land plant productivity and weathering strongly decreased, exerting negative feedback on aquatic productivity. Increased CO_2 concentrations were triggered by asteroid impacts and volcanic activity and in the Mesozoic era could be related to the gymnosperm flora with lower metabolic and weathering rates. A high O_2/CO_2 ratio is metabolically linked to the formation of citrate and oxalate, the main factors causing weathering, and to the production of reactive oxygen species, which triggered mutations and stimulated the evolution of land plants. The development of angiosperms resulted in a decrease in CO_2 concentration during the Cenozoic era, which finally led to the glacial-interglacial oscillations in the Pleistocene epoch. Photorespiration, the rate of which is directly related to the O_2/CO_2 ratio, due to the dual function of Rubisco, may be an important mechanism in maintaining the limits of O_2 and CO_2 concentrations by restricting land plant productivity and weathering.

Abbreviations: CCM – carbon concentration mechanism; ka – thousand years; Ma – million years; ppm – parts per million

Introduction

The atmosphere on Earth is in an extreme state of disequilibrium in which highly reactive gases, such as oxygen and methane, exist together at concentrations that are different by many orders of magnitude from the photochemical steady state (Lenton 1998). Living organisms regulate the composition of the Earth's atmosphere via large biogenic fluxes of gases (Lovelock 1972; Vernadsky [1926] 1998). These fluxes can be modelled by daisyworld (a model describing a very simple planet that has only two species of life on its surface – white and black daisies) scenarios, which are based on feedback regulation of the global environment (Watson and Lovelock 1983; Adams et al. 2003). The turnover of CO_2 and O_2 through the biosphere dramatically exceeds the turnover of inorganic

geochemical cycles. The annual flux of CO_2 through the biosphere is approximately 10% of the atmospheric CO_2, or slightly more than 0.1% of the total carbon in the biosphere. Thus the turnover time of atmospheric CO_2 is about 10 years, while the turnover of all carbon could be less than 1 ka (thousand years). Each year, 120 Pg (120×10^{15} g) of carbon is exchanged in each direction between terrestrial ecosystems and the atmosphere; another 90 Pg is exchanged between the ocean and the atmosphere, while 6.3 Pg is emitted by burning fossil fuels (Scholes and Noble 2001). For atmospheric O_2, the turnover time is 4.5 ka, while the inorganic cycle is approximately 3.2 Ma (million years) (Lenton 1998). Photosynthetic organisms producing O_2 and utilizing CO_2 have played a key role in regulating the gaseous content of the atmosphere, from their first appearance and continuing evolution. We analyse here the idea that the gaseous balance of the modern atmosphere, is adjusted mainly by the activity of land plants.

Gaseous content of the atmosphere during Phanerozoic

The Phanerozoic eon covers roughly $\sim$550 Ma back to the time when diverse hard-shelled animals first appeared (Figure 1). It is divided into three
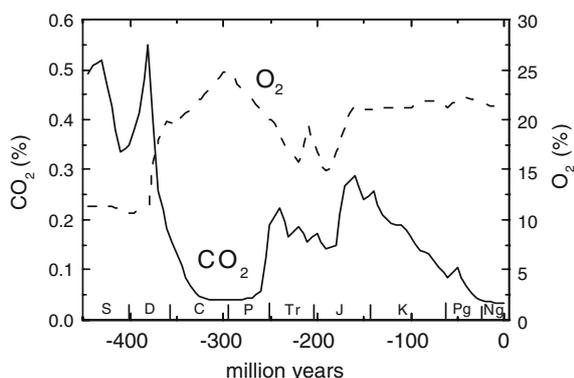
Figure 1. Changes in the atmospheric concentrations of CO_2 (solid line) and O_2 (dashed line) during the Phanerozoic eon. Abbreviation of the periods: S – Silurian, D – Devonian, C – Carboniferous, P – Permian (Palaeozoic era); Tr – Triassic, J – Jurassic, K – Cretaceous (Mesozoic era); Pg – Palaeogene and Ng – Neogene (Cenozoic era). The first two periods of Palaeozoic era (Cambrian and Ordovician) are not shown because of uncertainty in establishing the CO_2 and O_2 concentrations. The O_2 estimates are based on Lenton (2001), the CO_2 estimates are from the GEOCARB III model (Berner and Kothavala 2001).

eras – Palaeozoic, Mesozoic, and Cenozoic. The border between Phanerozoic and Precambrian eons (which includes the Proterozoic and Archaean eras) is clear-cut and corresponds to the first appearance of abundant metazoan fossils. The borders between Palaeozoic and Mesozoic ($\sim$245 Ma) and Mesozoic and Cenozoic ($\sim$65 Ma) eras are also well defined and are proven to correspond to major asteroid impacts (Ahrens and Jahren 2000; Benton and Twitchett 2003). The Palaeozoic era is divided into six periods (Cambrian, Ordovician, Silurian, Devonian, Carboniferous and Permian), and the Mesozoic era into three periods (Triassic, Jurassic and Cretaceous). The Cenozoic era is divided into seven epochs (Palaeocene, Eocene, Oligocene, Miocene, Pliocene, Pleistocene and Holocene). The first three are united as the Palaeogene period and the last four as the Neogene period. The previous classification considered the last two as a separate Quaternary period. The Holocene epoch started $\sim$12 ka ago and corresponds to the development of human civilization after the last ice age. There has been a suggestion of introducing a separate epoch (Anthropocene) (Crutzen 2002), which started with the industrial revolution (the exact time designated from the invention of the steam engine in 1784 by James Watt), corresponding to major anthropogenic effects, including the tremendous rise in atmospheric CO_2, which became evident only in the last century.

Concentrations of O_2 during Phanerozoic

Life originated in an anoxic atmosphere and the first available O_2 was produced by photosynthesis. The oxygenic photosynthesis of cyanobacteria is a very ancient process and probably appeared in the Archaean era, as early as 3800 Ma (Lenton 2001). The presence of O_2 sinks including photochemical destruction, reduced volcanic and metamorphic gases and continental weathering, prevented the rise of atmospheric O_2, until the sinks became saturated. After all the inorganic reductants had become exhausted, photosynthesis, which global overall rate is reflected in organic carbon burial, was needed for oxygen to accumulate in the atmosphere (Bjerrum and Canfield 2004). The O_2 concentration did not rise above 800 ppm until the middle Proterozoic (2200–2000 Ma), when it increased to 2000 ppm (0.2%) (Rye and Holland

1998). Later in the Proterozoic era, the O_2 concentration increased to values of 2–3% and rose again towards the end of Proterozoic (1000–570 Ma), probably triggering the Cambrian 'explosion' (the evolutionary diversification of large metazoans) (von Bloh et al. 2003), when it increased to more than 10%. The apparent diversification corresponding to the Cambrian explosion came from a sudden capacity of metazoans to be calcified and preserved as $CaCO_3$. There could be a significant diversification accompanying the rise of O_2 preceding the border between the Proterozoic and Cambrian, as the molecular clock data indicate (Knoll 1994). Biological colonization of the land surface began in the late Proterozoic, leading to phosphate and silicate weathering from rocks and a decreasing CO_2 concentration, while the O_2 concentration increased (Lenton and Watson 2004).

Existing geochemical models indicate an O_2 concentration of 15–17% in early Phanerozoic (Berner and Canfield 1989; Berner et al. 2000; Berner 2003a), however before the emergence of land plants, the O_2 concentration could have been as low as 12% during the period 570–400 Ma (Lenton 2001). With the appearance of land plants, which evolved 420 Ma and were widespread by 370 Ma, the O_2 concentration increased, reaching a peak near 300 Ma (late Carboniferous). Giant dragonflies, charcoal deposits and indications of intensive fires, provide evidence for concentrations of O_2 higher than present. Berner et al. (2000, 2003) have suggested a maximum of 35% O_2 in late Carboniferous, while more moderate estimates taking into account feedback of phosphorus weathering, give an upper limit of around 25% (Lenton 2001). After this period, the concentration of O_2 decreased and was relatively stable, falling during Triassic and Jurassic below 20% (with a corresponding disappearance of fires and charcoal burial) and increasing in Cretaceous (150 Ma) to the present day value or higher (Lenton 2001; Bergman et al. 2004) (Figure 1).

Although it is likely that 35% O_2 is too high an estimate, Wildman et al. (2004) have shown that even at such high O_2 concentration there would be no widespread burning of forests following a single lightning strike, at moisture contents common to living plants. Times of high O_2 agree with observations of fire-resistant plant morphology, large insects and high concentrations of fossil charcoal
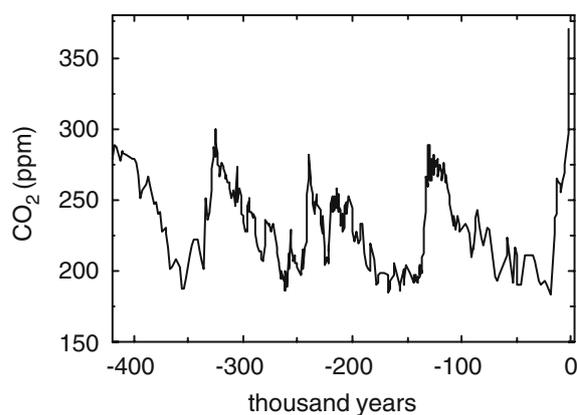
Figure 2. Glacial-interglacial oscillations of CO_2 concentration during last 420 thousand years (Petit et al. 1999). The 20th century CO_2 increase is also shown.

(Wildman et al. 2004). The latest estimates of the COPSE (Carbon–Oxygen–Phosphorus–Sulphur-Evolution) model (which couples four geochemical cycles as compared to earlier single cycle models) provide a value for O_2 in the Permo-Carboniferous of 30% with an upper limit of 33%. The COPSE model questions the low O_2 levels in the Triassic and the Jurassic, estimating them as nearer 20–22% (Bergman et al. 2004). The authors of the model, however, state that, although from 350 Ma to present day, the charcoal record offers the basis for the O_2 estimates, its interpretation relative to absolute O_2 concentrations still varies.

Concentrations of CO_2 during Phanerozoic

Modern geochemical modelling based on the distribution of ^{13}C and other isotopes, shows that before the fall in CO_2 caused by the appearance of land plants, the concentration of CO_2 was 0.4–0.5% at the beginning of the Phanerozoic era in the Ordovician and in the Cambrian. The CO_2 concentration dropped down during the Devonian and the Carboniferous (coinciding with the highest O_2 concentration in the late Carboniferous). It was higher during the Mesozoic era, probably reaching 2000 ppm (0.2%) in some periods (up to 1400 ppm in the COPSE model, Bergman et al. 2004). Later in the Cenozoic era, a gradual decrease of CO_2 took place and for nearly 50 Ma the concentration was not much higher than the present preindustrial level of 300 ppm (Royer et al. 2001a, b). Detailed analyses of the air bubbles in cores of Antarctic ice have indicated that

the CO_2 concentration oscillated between 180 and 280 ppm, during the last 420 ka (Figure 2) (Petit et al. 1999; Cuffey and Vimeux 2001). The data has been obtained for the 740-ka period showing eight glacial cycles (EPICA community members 2004). These oscillations were of a 100 ka period, with a slow fall and a rapid increase (less than 10 ka). Ten to fifteen smaller oscillations with the amplitude of 10–20 ppm were observed within every large oscillation. A similar occurrence of oscillating CO_2 with corresponding glaciations and deglaciations, probably also took place around the Carboniferous-Permian boundary (Di Michele et al. 2001).

The evaluation of atmospheric CO_2 based mainly on $\delta^{13}C$ values of pedogenic carbonates provides a good CO_2 estimate for the pre-Cenozoic period but does not resolve short-term excursions of 5–10 Ma. For the Cenozoic, the delta ^{13}C of the organic remains of phytoplankton could be of use, both for temporal resolution (up to 1–10 ka) and calculated CO_2 concentrations (Royer et al. 2001a). At elevated CO_2 concentrations as detected in the Mesozoic, this method is not useful, it also needs corrections for changes in growth rate and O_2 concentration. Significant concerns have been raised about the use of isotope palaeobarometry even at moderate CO_2 concentrations (Laws et al. 2002) and the proponents of this method now state that the palaeobarometric data can only be used for a rough estimate of CO_2 concentration (Rau et al. 1996, 1997; Royer et al. 2001a).

In Berner's GEOCARB models, the latest being GEOCARB III (Berner and Kothavala 2001), the isotopic data are used with corrections for different factors (mostly due to the rates of weathering, but also to global degassing and mountain uplift), to obtain a reliable model of CO_2 changes during Phanerozoic. Models of CO_2 in the atmosphere based on stomatal densities of fossil leaves (Figure 3) (Retallack 2001), show more precise timing for outbursts of CO_2 caused e.g. by asteroid impacts, which took place at the Permian–Triassic, Triassic–Jurassic and Cretaceous–Palaeogene boundaries, also some smaller events which occurred throughout Phanerozoic. Stomata adapt to local and global changes on all timescales (Hetherington and Woodward 2003). The measurement of fossil stomatal densities provides excellent temporal resolution (less than 100 years), with high precision at low CO_2 but
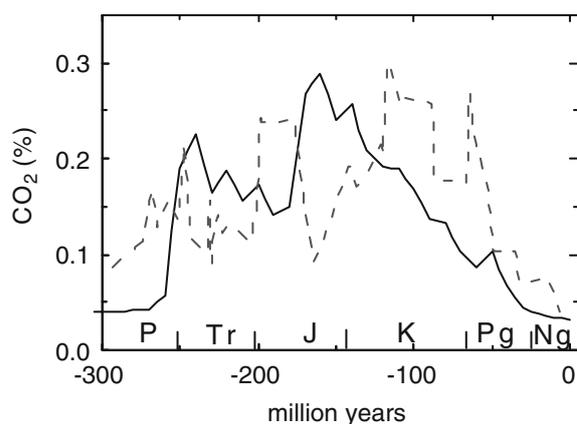
Figure 3. Changes in the atmospheric CO_2 concentrations over 300 million years. The CO_2 values are taken from the GEO-CARB III model (Berner and Kothavala 2001) (solid line) and from stomatal indices (Retallack 2001) (dashed line). Abbreviations of the geological periods are as in Figure 1.

losses of sensitivity at higher concentrations (Royer et al. 2001b).

Temperature

The deviations in the temperature of the Earth's atmosphere can be correlated with the CO_2 concentration by the equation (Kothavala et al. 1999):

$$\Delta T = 4 \ln(RCO_2) \tag{1}$$

where RCO_2 is the CO_2 concentration expressed as a ratio to the preindustrial CO_2 level (290 ppm).

The data based on foraminifer shells extracted from impermeable clay-rich sediments, show that the distribution and replacement of the species of these temperature-sensitive organisms in clay-rich sediments during late Cretaceous and Eocene epochs is in agreement with the variations in CO_2 concentrations (Pearson et al. 2001). Correlations between temperature and CO_2 concentration during the last 400 ka have been shown to be very precise (Cuffey and Vimeux 2001). Some deviations in earlier periods have been demonstrated, e.g. in Miocene, where the medium temperatures were 6 °C higher than predicted from a CO_2 concentration of 250–290 ppm, which could be explained by the presence of other greenhouse gasses, e.g. methane (Zachos et al. 2001).

We have used Equation (1) and the estimates of CO_2 from the GEOCARB III model to calculate the mean surface temperature-deviations during

the Phanerozoic eon, whilst taking into consideration the 5% increase in the brightness of the sun from the Proterozoic era to present (Tajika 2003). From the data on O_2, CO_2 and temperature, we can conclude that these parameters stabilised following the appearance of land plants, with concentrations in the range of 17–30% for O_2, 0.02–0.2% for CO_2 and average temperatures ~3 °C higher (with the deviation of 3–4 °C) than present day (Figures 1 and 4).

Land plant photosynthesis and O_2/CO_2 balance

In the photosynthesis process, CO_2 is fixed via the Calvin–Benson cycle, in which ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco) is the primary CO_2 assimilatory enzyme in C_3 plants. During evolution, the enzyme somewhat surprisingly, has preserved a capacity to use O_2 as a substrate, which in an atmosphere of high O_2 and low CO_2, makes CO_2 fixation less efficient due to the photorespiratory process, starting with the oxygenation reaction of Rubisco (see below). Metabolic pathways have evolved to overcome the loss of CO_2 during photorespiration, either via a CO_2 concentrating mechanism (CCM) in algae, or via the C_4 pathway of photosynthesis in some advanced higher plants. In the latter, primary CO_2 fixation is carried out by another enzyme (phospho*enol*pyruvate carboxylase), which has no
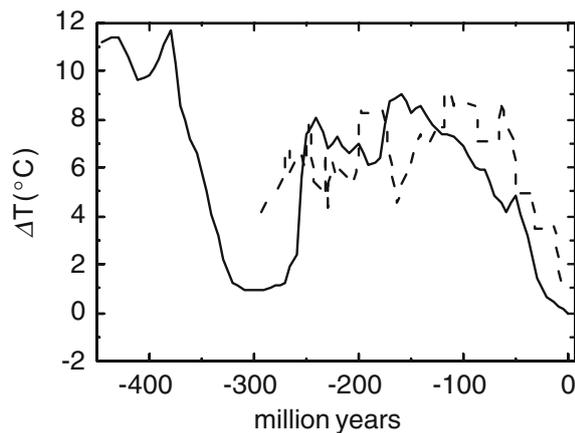
Figure 4. Average temperature changes (ΔT) during the Phanerozoic eon according to CO_2 data obtained from the GEO-CARB III model (solid line) and from the averaged data of stomatal indices (dashed line). Calculated from Equation (1) based on the estimates of Berner and Kothavala (2001) and Retallack (2001).

oxygenase reaction and CO_2 is delivered to the Calvin–Benson cycle at a higher concentration in a specific compartment. We have discussed below, the biospheric consequences of the development of photosynthesis on Earth and its role in preserving the O_2/CO_2 balance.

The dual function of ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco)

The Rubisco enzyme has maintained during evolution the affinity for oxygen, although there is evidence of its reduction in some species (Bird et al. 1982). This activity becomes physiologically important in the atmosphere with low CO_2 and high O_2 causing the photorespiration process. The Rubisco specificity factor (Laing et al. 1974), which defines the preference of Rubisco for CO_2 compared to O_2 is:

$$\tau = V_c K_o / K_c V_o \qquad (2)$$

where K_o is the Michaelis constant for O_2, K_c is the Michaelis constant for CO_2, V_c is the maximal rate with CO_2, V_o is the maximal rate with O_2.

The value of τ is about 100 at 25 °C in the angiosperm C_3 species, while it is lower in C_4 plants, in conifers and in ferns, and it is significantly lower in some green algae (Jordan and Ogren 1981, 1983). If we consider the O_2/CO_2 ratio in the atmosphere, which is about 36 times higher than in solution at 25 °C because of higher solubility of CO_2 compared to O_2, we get a value for the specificity factor of Rubisco of about 3600 in relation to the atmospheric O_2/CO_2 ratio. This indicates that the Rubisco enzyme will have a 3600 times higher affinity for CO_2 than for O_2 in the atmosphere, provided there are no limitation effects of stomatal conductance. In the real situation in plants, we have to consider also the concentration of CO_2 near the sites of carboxylation, which can be ~50% less than that in the air (Evans and von Caemmerer 1996), or even less for xeromorphic plants (Di Marco et al. 1990), for estimating the specificity of Rubisco in the surrounding atmosphere.

Only the unusual Rubisco enzymes from certain thermophilic red algae (cyanidiophytes) have very high carboxylation to oxygenation (V_c/V_o) ratios (Uemura et al. 1997), which can be explained by a higher affinity for CO_2, rather than a lower affinity for oxygen. However the τ values

of the cyanidiophytes are much less extreme when the *in vitro* assays for τ are conducted at the growth temperatures of the organisms (Uemura et al. 1997). The Rhodophyta species living at moderate temperatures have Rubisco with much less variation in τ values (Uemura et al. 1997), while the highest τ value (310 at 90 °C) was reported for the Rubisco of the hyperthermophilic archaeon, *Pyrococcus kodakaraensis* (Ezaki et al. 1999).

On the other hand, Tortell (2000) has shown that plotting the Rubisco specificity factor for a range of algae against date of evolution, gives a good correlation (showing the increase of τ during the course of evolution) and the red algae really stand out as having different τ values. However, the question why this high affinity enzyme was not positively selected for, during the evolution of other groups leading to the appearance of land plants, still remains open. It has been shown that the Form 1 Rubisco from red algae is expressed abundantly in transgenic higher plant chloroplasts but is not assembled to form an active enzyme (Whitney et al. 2001). However, it has been possible to express active bacterial Rubisco enzymes in higher plants and the CO_2 assimilation parameters of these plants correlated with the kinetic properties of the inserted Rubisco enzyme (Parry et al. 2003; Whitney and Andrews 2003). A higher specificity factor of Rubisco in some C_3 plants (e.g. in sunflower by 30%), leads to a marked increase in net photosynthesis and biomass accumulation (Kent et al. 1992; Kent and Tomany 1995).

The specificity factor of Rubisco can impose limits on the CO_2 and O_2 concentrations in the atmosphere. Without special concentrating mechanisms for CO_2, plants can only exist in a range of specified concentrations of O_2 and CO_2. Above a certain concentration of O_2 and below a certain concentration of CO_2 (compensation points), the oxygenase reaction of Rubisco will dissipate more carbon than is fixed in the carboxylase reaction (Tolbert et al. 1995). Even small changes in the concentrations of O_2 and CO_2 in the atmosphere, can lead to drastic changes in metabolism, favouring either reductive or oxidative reactions (Tolbert et al. 1995; Cen et al. 2001).

At low CO_2 levels, the CO_2 concentrating mechanisms (CCM) become important (Badger and Price 2003). The CCMs evolved as a response to the decrease in CO_2 concentration during Paleozoic. The CCMs use energy for the active transport of protons, CO_2 or bicarbonate. Some CCMs can work with acid-catalysed bicarbonate conversion to carbon dioxide in a compartment in which the equilibrium carbon dioxide concentration is greater than that in the bulk phase (Badger and Price 2003). To this compartment, bicarbonate can diffuse from the bulk phase (Walker et al. 1980), where the energisation of the CCM operates on the basis of extracellular acid zones produced by the plasmalemma ATPase.

Difference in photosynthesis of aquatic and land plants

In algae, high rates of photosynthetic carbon assimilation occur even at CO_2 concentrations as low as 5 ppm, because of an effective CO_2 concentrating mechanism (CCM), based on carbonic anhydrase (Raven 2003). This mechanism is induced by low CO_2 concentrations, being preceded by photorespiratory release of glycolate (and to lesser extent glyoxylate, glycine and CO_2). The rate of photorespiratory decarboxylation of glycine is low in algal cells, due to the operation of a CCM, thus preventing the loss of essential ammonia (Ramazanov and Cardenas 1992; Igamberdiev and Lea 2002). The data showed that the C_3 land plants lose ammonia from the leaves at a rate in the order of 0.1–1 nmol m^{-2} (leaf area) s^{-1} and this rate increased with temperature and nitrogen nutrition (Husted et al. 2002). The leaves also exhibit a compensation point for ammonia, which ranges from 0.1 to 20 nmol mol^{-1} in air (Schjoerring et al. 2000). Due to the very high water solubility of ammonia, its loss by aquatic plants would deplete them in nitrogen very rapidly. So, in contrast to land plants, the role of peroxisomes in photorespiration in algae is not very important, photorespiratory peroxisomes with the same enzyme content as in land plants appeared only in their immediate ancestors, the Charophyceae (Huss and Kranz 1997; Karol et al. 2001).

The CO_2 enrichment caused by a CCM decreases the degree of ^{13}C fractionation carried out by Rubisco, while in ambient CO_2 concentrations this fractionation is usually comparable with the values characteristic for C_3 higher plants (Kaplan and Reinhold 1999). Ambient CO_2 is not sufficient to completely repress CCMs in most

algae; large discrimination against ^{13}C can be found at very high CO_2 and low growth rates. Thus in algae, in contrast to C_3 land plants, assimilated carbon is characterized by a decrease in ^{13}C fractionation with decreasing CO_2 concentration (Laws et al. 2002). On this basis, Rothman (2001, 2002) estimated the atmospheric CO_2 concentration during the Phanerozoic period, which is in a good agreement with other models, except that it does not predict a lower CO_2 levels in Carboniferous-Permian suggested by the GEO-CARB models. This can be explained by the non-inclusion of the effects of O_2 concentration on ^{13}C fractionation. An elevation in O_2 causes in algae, in a similar manner to land plants, an increase in the rate of ^{13}C fractionation (Berner et al. 2000). In C_3 land plants, lowering the CO_2 concentration leads to the opening of stomata, thus decreasing the effect of stomatal conductance on ^{13}C fractionation (Igamberdiev et al. 2004). Photorespiration itself contributes to carbon isotope fractionation (Igamberdiev et al. 2004), and it is likely that the O_2/CO_2 ratio was the main factor determining the carbon isotope composition of C_3 land plants during the Phanerozoic eon (Strauss and Peters-Kottig 2003).

The absence, or very low activity of a CCM and active peroxisomal metabolism together with a high glycine decarboxylase capacity in mitochondria, has made the photorespiratory process very intensive in land plants. Initially, the marine phytoplankton always had a higher biomass and higher rates of photosynthesis than land plants. A higher global rate of photosynthesis does not necessarily mean higher biomass in the case of phytoplankton; today there are similar primary productivities in the sea and on land (Müller-Karger et al. 2005), yet there is about three orders of magnitude less primary producer biomass in the ocean than on land due to a much greater turnover of primary producers in the ocean. New satellite observations have shown that phytoplankton productivity is even higher than earlier estimates (Behrenfeld et al. 2005).

The role of phytoplankton in O_2 release was significant from the time when all inorganic reductants had been exhausted and organic carbon burial began to take place (Bjerrum and Canfield 2004), while CO_2 depletion was probably mostly due to the activity of land plants via weathering (Berner 1997), although the direct role of photo-

synthesis in this process remains to be quantified. When the CO_2 concentration in the atmosphere decreased to the minimum corresponding to the ecological compensation point in land plants, the productivity of land plants diminished. The ecological compensation point is a CO_2 concentration (in average 150–180 ppm at 21% O_2) below which plants are unable to complete their lifecycles (Sage and Coleman 2001). During glacial periods, temperature gradients drive oceanic circulation causing a greater supply of oxygen to deep waters (Berner 2003a). This would lead to an increase in atmospheric carbon dioxide via inhibition of the formation of anoxic waters in the bottom layers and a reduction of organic burial (Berner 2003a).

Respiration and photorespiration

The reduction level of higher plants (reflecting the reduction state of reaction centres in chloroplasts and pyridine nucleotides in all subcellular compartments, primarily in mitochondria) is strongly affected by the O_2/CO_2 ratio. At low CO_2 and high O_2, the overreduction of chloroplast reaction centres occurs, due to the low rate of CO_2 fixation in the Calvin cycle. Under these conditions, photorespiratory ammonia assimilation together with other energy utilizing and/or wasting processes, consume the excess reduction power in the chlo-
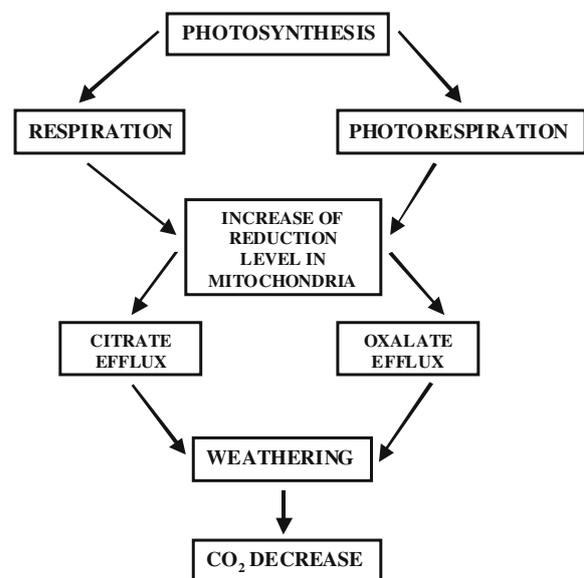
Figure 5. Land plant metabolism and excretion of organic acids.

roplasts (Givan et al. 1988; Heber et al. 1996; Osmond et al. 1997; Igamberdiev et al. 2001; Igamberdiev and Lea 2002). In addition, in the mitochondria, photorespiration and respiration increase the reduction level (moderated by the operation of non-coupled pathways). This results in the incomplete oxidation of glycolytic and photorespiratory substrates leading correspondingly to the efflux of citrate from mitochondria (Igamberdiev and Gardeström 2003) and to the suppression of glycine oxidation resulting in oxalate formation in peroxisomes (Igamberdiev and Lea 2002), both compounds being further excreted into the soil (Figure 5).

Photorespiration is essential even at much higher atmospheric CO_2 concentrations than at present. High CO_2 concentrations result in an elevation of temperature, which increases photorespiration and dark respiration rates more than the rate of assimilatory carboxylation (Brooks and Farquhar 1985). However, the development of large leaves may have prevented overheating due to higher transpiration rates (Beerling et al. 2001). Based on the temperature dependence of the oxygenase to carboxylase ratio of Rubisco (Brooks and Farquhar 1985; Bernacchi et al. 2001) and the estimated deviations of surface temperature from the mean value, we can calculate the oxygenase to carboxylase ratio during Phanerozoic according to Berner's estimate of CO_2 and Lenton's estimate of O_2 in the atmosphere. The ratio of photorespiratory rate to photosynthetic assimilation rate is half of the oxygenase to carboxylase ratio (Sharkey 1988). Palaeozoic photorespiratory rates could be slightly higher as the carboxylase function of Rubisco was lower by 10–20% (Bird et al. 1982), but these rates could also respond to a lower brightness of the sun ($\sim$5%), which would result in lower temperatures (Tajika 2003).

Land plant photosynthesis and photorespiration in the regulation of O_2 and CO_2

Tolbert et al. (1995) developed the concept that CO_2 depletion/O_2 release caused by photosynthesis is counterbalanced by CO_2 release/O_2 uptake during photorespiration. Tolbert et al. proposed that the equilibrium establishes at concentrations of CO_2 and O_2 near the preindustrial level. In an experiment with tobacco and spinach in closed chambers, assimilation of CO_2 led to its relative

exhaustion down to low concentrations and to an increase of O_2 with the establishment of an equilibrium O_2/CO_2 ratio (Tolbert et al. 1995). The equilibrium concentration of O_2 was established at 23% with a CO_2 concentration of 220 ppm – which is close to the glacial CO_2 level. The CO_2 concentration of 350 ppm was in equilibrium with 27–28% O_2 and the CO_2 concentration of 700 ppm was in equilibrium with 35% O_2. These values indicate that in the Permo–Carboniferous boundary, a predicted CO_2 concentration of 300–350 ppm (Berner 1997; Beerling et al. 2001; Beerling 2002) would correspond with the moderate estimate of O_2 concentration ($\sim$25%) made by Lenton (2001), which takes into account phosphorus weathering, rather than the more extreme (35%) value proposed by Berner (2003a, b). However, some experiments have shown that it is possible for plants to complete their lifecycles even at 35% O_2 and 350 ppm CO_2 (Beerling and Berner 2000).

The latest estimate of O_2 and CO_2 concentrations based on the COPSE model (Bergman et al. 2004), uniting earlier GEOCARB (Berner and Kothavala 2001) and the feedback-based atmospheric O_2 model (Lenton 2001), suggests even higher late Carboniferous CO_2 levels, closer to 800–900 ppm. With the suggested high late Carboniferous O_2 levels, this fits nicely with the O_2/CO_2 equilibration by land plants suggested by Tolbert et al. (1995). The COPSE model also gives higher O_2 levels for the late Mesozoic (Cretaceous) (30% and above), which agrees well with the suggested equilibration at high CO_2 concentrations ($\sim$1000 ppm) estimated for that time.

In our view, the approach taken by Tolbert et al. (1995) is of value as long as it is remembered that the experiments were carried out in closed chambers over short periods of time, and therefore have some limitations when applied to the whole biosphere. The enclosed system lacked an ocean and a rock cycle, both of which regulated the atmospheric CO_2 during the evolution of land plants. To work well, the mechanism proposed by Tolbert et al. (1995) should provide a faster and more efficient O_2/CO_2 equilibration in the atmosphere as compared to other factors, especially the oceanic one. In O_2 evolution, the role of photosynthesis (both marine and land) was clearly predominant, but the role of different factors in CO_2 depletion/evolution, requires numerous contro-

versial estimates. The inclusion of the ocean in estimates of CO_2 production by marine phytoplankton (Raven and Falkowski 1999) can explain the rapid recovery from glacial low CO_2 concentrations, however the CO_2 depletion is always a slower process.

It took many millions years in Palaeozoic to deplete CO_2 during the emergence of land plants and this took place via a weathering process (Berner 1997), rather than direct photosynthetic assimilation. After asteroid impacts, the depletion of excess CO_2 took hundreds of thousands or even millions of years (McElwain et al. 1999; Ahrens and Jahren 2000) and the interglacial rise of CO_2 occupied almost a hundred thousand years (Falkowski et al. 2000). All this means is that a simple photosynthetic/photorespiratory O_2/CO_2 balance mechanism is not sufficient to explain gaseous homeostasis of the atmosphere. Even together with other biospheric processes, it is not able to respond to dramatic changes such as the industrial rise of CO_2, over short time periods (Berner 2003a).

However, land plant photosynthesis does mediate the main processes of CO_2 depletion such as weathering and the ocean sink and this depletion never falls below the ecological CO_2 compensation point, i.e. the feedback mechanisms switch upon depletion, resulting in a rise of CO_2. Thus the biospheric equilibrium of CO_2/O_2 concentration works with a feedback mechanisms that may be responsible for the oscillatory regime, probably together with synchronization of these oscillations with the cycles of solar activity. This indicates that the approach of Tolbert et al. (1995) has a rational basis and requires further development and clarification to explain the observed biospheric phenomena.

The role of weathering by land plants in CO_2 depletion in the atmosphere

It has been suggested that the removal of CO_2 from the biosphere occurs more via the weathering of silicates and formation of carbonates, during root activity and soil formation, rather than via photosynthetic assimilation (Berner 1997). The plant activity in this process is apparently more important than are temperature and rainfall. The weathering process is directly connected with the photosynthetic activity of land plants and a

requirement for phosphate, being caused mainly by the excretion of citrate and oxalate from roots (Diatloff et al. 2004). Oxalate is formed as a side product of the glycolate oxidase reaction in leaves, when the reduction level in mitochondria established during high rates of photorespiration, suppresses the oxidation of glycine (Igamberdiev and Lea 2002). Other pathways of oxalate formation that occur in plants, involve isocitrate lyase that may also operate in the cytosol (Igamberdiev et al. 1986), oxaloacetate lyase (Raven et al. 1982), and the catabolism of ascorbate (de Bolt et al. 2004; Green and Fry 2005). These pathways are not linked directly to photorespiration but they relate to high photosynthetic and respiratory activities. Citrate is also formed when the reduction level in mitochondria increases, due to switching from the complete to the partial TCA cycle (Igamberdiev and Gardeström 2003). Organic acids can be transported to roots, or alternatively citrate can be formed in roots due to high activities of citrate synthase (Kihara et al. 2003). At the pH of phloem sap, oxalate salts are transported together with citrate (which constitutes one third of all acids transported) and malate. The transport through the phloem flow together with the formation of organic acids in the rhizosphere constitutes an effective mechanism of organic acid excretion by the root system (Jones 1998).

In the weathering process, citrate and oxalate release phosphate and other mineral compounds, during soil formation. The release of phosphate led to the eutrophication of the ocean and to the increase of photosynthetic productivity by algae, as well as to the substitution of silicates by carbonates, both processes consuming atmospheric CO_2 (Lenton 2001). The weathering was more intensive than the release of CO_2 to the atmosphere due to geological and biological activities including fires and respiration in extended periods, except during the short times of volcanic eruptions etc. This led to a decrease in the atmospheric concentration of CO_2 up to the time of glaciation, when the CO_2 production rate increased. Glaciation strongly decreased the process of weathering (due to both lower rates of metabolism in the cooler and drier climate and less plant cover) and the CO_2 concentration began to rise mostly via negative feedback on oceanic phytoplankton, which release CO_2 more intensively as the CO_2 concentration falls (Raven 1994, 2000; Raven and Falkowski 1999;
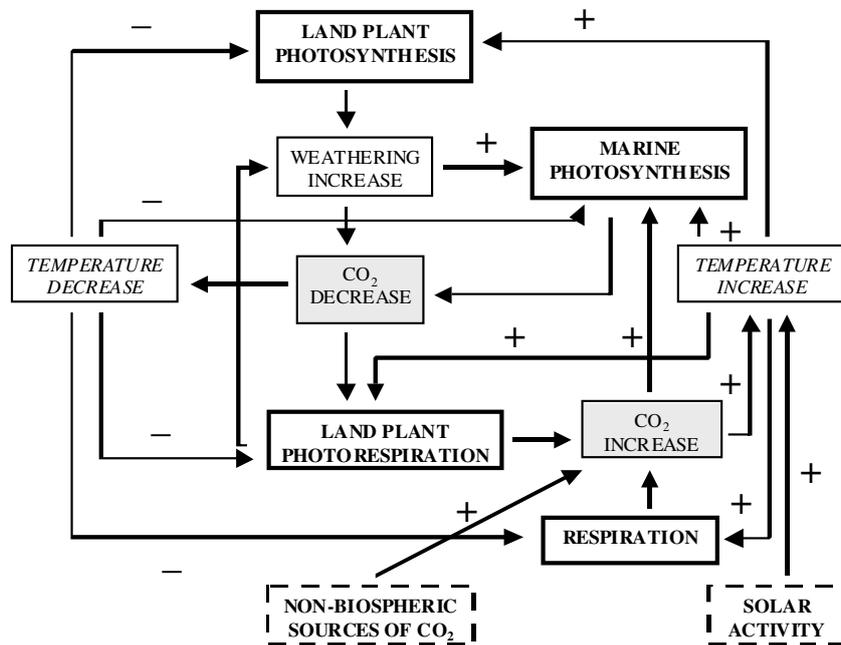
Figure 6. Factors affecting CO_2 balance in Earth's atmosphere.

Riebesell et al. 2000). At low CO_2 concentration, fast-growing grasslands are predominant, while when the CO_2 increases, slower growing trees become widespread (Bond et al. 2003), contributing to different rates of weathering and CO_2 production. In simulation experiments with changing temperature in enclosed environments, it was shown that at higher temperatures the release of CO_2 increases sharply (Gerber et al. 2004).

Vascular plants amplify the rate of weathering by about an order of magnitude relative to lichens and mosses (Lenton 2001). Photosynthetic uptake of CO_2 (and release of O_2) (currently 8.4×10^{15} mol y^{-1}) is counterbalanced by respiration (and photorespiration in land plants) (currently 8.39×10^{15} mol y^{-1}). The photosynthesis process will deplete CO_2 if burial of organic C takes place, the rate of which is currently 10^{13} mol y^{-1} and was higher in the periods with elevated CO_2 concentrations at the Permian–Carboniferous boundary (Lenton 1998, 2001). The opposite process (organic carbon weathering and degassing) is estimated to be approximately the same rate as photosynthetic CO_2 assimilation, but this is a matter of debate, especially for earlier times, e.g. late Devonian and Carboniferous (Lenton 2001). Thus it is difficult to estimate the relative input of

Tolbert's factor (photosynthesis/photorespiration balance) and Berner's factor (silicate weathering) on CO_2 depletion. But even if depletion of CO_2 is mainly due to silicate weathering, it would take place down to values comparable with the existence of land plants, and then feedback processes would start to act. Interactions of CO_2 forming and CO_2 depleting factors may contribute to the glacial-interglacial oscillations (see below). If burial of carbon takes place, as in the Carboniferous, or a total increase of biomass takes place as in the interglacial periods, this will also be a cause of CO_2 depletion. Probably the initial depletion was mainly due to the weathering process, while near the CO_2 minimum/O_2 maximum, the depletion is mainly due to photosynthetic assimilation. Near this critical point, plants at lower latitudes and also altitudes (at higher temperatures) will produce CO_2 while at higher latitudes (lower temperatures) they will consume it, but this will be limited by the decrease in temperature. Together with the uptake of CO_2 by the ocean, the processes of CO_2 assimilation and CO_2 release would have contributed to the glacial-interglacial oscillations (see Sigman and Boyle 2001), which were also synchronized with solar activity (Rial 2004).
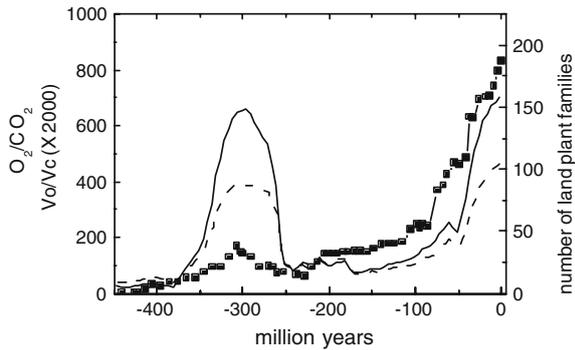
Figure 7. Time course of changes in the O_2/CO_2 ratio in the atmosphere during the Phanerozoic eon (solid line) based on the GEOCARB III model (Berner and Kothavala 2001), of the oxygenase to carboxylase ratio of Rubisco (dashed line) (calculated from the O_2/CO_2 ratio and the effects of temperature) and of the number of land plant families (squares) (Rothman 2001) over the Phanerozoic eon.

Figure 6 shows the global effects of the biosphere on the balance of CO_2 in the atmosphere, which includes photosynthetic CO_2 assimilation, photorespiration, weathering, temperature etc. For the modelling of these events, it is necessary to know the rate constants of all the processes and their dependence on temperature and CO_2 concentrations. The removal of CO_2 by weathering and by direct photosynthetic activity can be estimated from the relative flux intensities of these processes. At the present time, this information is incomplete.

At the junction of the Carboniferous and Permian periods, plant diversity decreased (Figure 7). This decrease was also affected by the strongest asteroid impact at the Permian–Triassic boundary (Benton and Twitchett 2003). During the Mesozoic era, the weathering process was probably less intensive because of the type of flora (gymnosperm) that existed (Moulton et al. 2000). This could correspond to higher concentrations of CO_2. The distribution of angiosperms in the Cretaceous could cause further increase of weathering and a decrease of CO_2 in the atmosphere.

O_2/CO_2 compensation ratio

An introduction to the concept of the compensation point (Γ) is needed, because it is established both by the CO_2 and the O_2 concentration. The CO_2 compensation point is determined as the concentration of CO_2, when the rate of photo-

synthetic CO_2 assimilation is equal to CO_2 release by respiration and photorespiration. If we ignore leaf respiration, which is relatively low in the light and probably does not exceed 5% of the rate of assimilation (Atkin et al. 2000), we get gamma star (Γ^*), the compensation point taking into consideration only photorespiration. Definitions of the CO_2 compensation point are based on a constant O_2 concentration, as it has been shown that the dependence of Γ on O_2 is linear (Farquhar et al. 1980). The value of Γ for C_3 plants at 21% O_2 is about 50 ppm CO_2 at 25 °C.

However, the real ecological compensation point is higher (because of the necessity of photosynthetic and respiration costs for maintenance, growth and productivity), being in general about 180 ppm depending on temperature, irradiance, humidity and other factors (Sage and Coleman 2000). Respiration by plant and non-plant organisms may contribute to the value of the ecological compensation point or at least have some feedback impact on the decrease of the atmospheric CO_2. Below some lesser CO_2 value than the ecological compensation point (at the O_2 value 21%), plants are unable to complete their lifecycles (Sage and Coleman 2000). Lack of carbon reduces the capacity of plants to assimilate nutrients, particularly nitrogen (Andrews et al. 2004). In addition, Tolbert et al. (1995) introduced the definition of O_2 compensation point, which means the concentration of O_2 at a constant concentration of CO_2, when the assimilation and the release of CO_2 are equal (Goyal 2001).

Combining both definitions, we get the definition of O_2/CO_2 compensation ratio, which represents the ratio of O_2 concentration to CO_2 compensation point at this concentration. For $\Gamma = 50$ ppm CO_2, the O_2/CO_2 compensation ratio is 21% $O_2/50$ ppm $CO_2 = 4200$. However, the ecological O_2/CO_2 compensation ratio (considering ecological compensation point of 180 ppm) is about 1200. This is probably the maximum ratio that occurred in the Carboniferous–Permian time and the Pleistocenic glacial times.

The value of the compensation point for CO_2 strongly depends on temperature (Jordan and Ogren 1983, 1984). The average temperature can be calculated approximately from the CO_2 concentration (see below) and the way that it changed during Phanerozoic can be seen in Figure 4. The temperature dependence of the compensation

point was originally proposed to be linear (Brooks and Farquhar 1985), now it is assumed to be exponential, which is more expressed upon the increase of temperature (Bernacchi et al. 2001). We can use the dependence suggested by Brooks and Farquhar (1985) (which approximates well over the moderate mean temperature values of the Earth's surface) to determine the effects of temperature changes on the ratio of O_2 and CO_2 concentrations, which is reflected in the value of the compensation ratio and in the rate of photorespiration.

An estimate of the V_o/V_c ratio of Rubisco (Figure 7), taking into account the effect of temperature, shows that it changed slightly less drastically during the past 350 Ma, than the O_2/CO_2 ratio. Since variation in the O_2/CO_2 ratio regulated by temperature is somewhat higher than that estimated by Brooks and Farquhar (1985), and since respiration (not included in our calculation) also increases drastically with a temperature rise, the real change of V_o/V_c will be 5 times or even less, while the O_2/CO_2 ratio changed more than ten-fold, being quite low during long periods of the Mesozoic era. At higher temperatures, the effects of O_2 (e.g. photoinhibition due to a higher reduction level in the chloroplast) will be pronounced even at higher CO_2 concentrations. During an increase of CO_2 in the atmosphere (as in Mesozoic), which corresponds to a higher mean temperature according to Equation (1), the O_2/CO_2 compensation ratio will be lower, than under depletion of CO_2 (this was actually observed in Earth's history).

Evolution of land plants and evolution of the atmosphere

Correlation of O_2 and CO_2 in the atmosphere with the evolutionary process

If the diversity of land plants expressed as the number of land plant families according to Rothman (2001) and Benton (1993), is compared with the concentrations of O_2 and CO_2 in the atmosphere, there is no obvious correlation between the diversity and concentration of either O_2 or CO_2. However, there is a surprisingly good correlation between the O_2/CO_2 ratio in the atmosphere and biodiversity (Figure 7). The correlation is even better if biodiversity is plotted against the effective O_2/CO_2 ratio (ratio of oxygenase to carboxylase rates of Rubisco, V_o/V_c), calculated on the basis of the effect of temperature on the compensation point according to Brooks and Farquhar (1985). It can be seen that the increase in this ratio correlates well with diversity, while a decrease accompanied the extinction of land plant families. A similar correlation has been observed with the number of animal species (Rothman 2001), which has not been discussed in this paper. Elevation of CO_2 under constant O_2, i.e. a decrease of the O_2/CO_2 ratio, has previously been shown to reduce biodiversity in land communities (Zavaleta et al. 2001, 2003a, b; Shaw et al. 2002).

However, the diversity of marine fauna has been shown to follow directly the CO_2 concentration and corresponding temperature changes (Cornette et al. 2002), while some parameters of plants are correlated directly with O_2 but not to CO_2, e.g. the replacement of woodiness by herbaceousness in evolution and the woodiness indices of plants (Gottlieb et al. 1995; Gottlieb and Borin 1998). In addition, it has been proposed that the evolution of secondary metabolites was triggered by O_2, providing the incorporation of oxygen atoms into a series of molecular species (Gottlieb and Borin 1998).

The increase in biodiversity during late Devonian and early Carboniferous corresponded to the increase in O_2/CO_2 ratio, peaking at the late Carboniferous–Permian boundary. This was the period of highest diversity of land plants before the late Mesozoic. The diversity could be even higher, since e.g. angiosperms became distributed widely only in Cretaceous, but comparisons of gene sequences showed that the differentiation between gymnosperms and angiosperms arose at the Carboniferous–Permian boundary (Savard et al. 1994). A Carboniferous–Permian high O_2 episode might have triggered this split between major plant groups. Although carbon isotope-based estimates show an average concentration of CO_2 of 0.3–0.4% in this period, recent data has indicated the existence of oscillations of CO_2 (and consequently temperature) of a 100 ka period (Sigman and Boyle 2001), possibly with minimum CO_2 concentrations (corresponding to glaciations) close to that in the Pleistocenic oscillations (Tajika 2003). There is also some indication of the appearance of C_4-like plants in the late

Carboniferous period based on the $\delta^{13}C$ value (19‰) of some fossils (Jones 1994) but this needs further substantiation.

The evolution of land plants was accomplished by the appearance and development of stomata. The stomata evolved in Silurian and the stomatal index increased as carbon dioxide decreased from the Silurian to the Carboniferous (Royer et al. 2001a). The decrease in CO_2 and increase of O_2 led to the importance of maximizing CO_2 diffusion into the leaf (Beerling and Woodward 1997), thereby raising intercellular CO_2 concentrations and reducing CO_2 evolution by photorespiration. In addition, high transpiration rates prevented the overheating of leaves, allowing the evolution of larger leaves (Beerling et al. 2001).

The decrease in O_2/CO_2 ratio during Permian was accompanied by a decrease in the diversity of land plants. The asteroid impact event of the Permian–Triassic boundary, the greatest in the history of Phanerozoic, completed this process destroying 90% of the marine animal species and 70% of the plant species (Rothman 2001). While all impact events, after a short period of cooling, led to global warming and a rise in atmospheric CO_2, this rise probably determined the relatively low diversity of the Triassic period. The determination of atmospheric CO_2 concentrations based on stomatal characteristics, shows the periods of instant CO_2 increase caused by the impacts of asteroids, more clearly than the isotopic data (Retallack 2001). This can be seen at the boundaries of Permian–Triassic, Triassic–Jurassic and Cretaceous–Palaeogene (Figure 3).

Plant metabolism can be more reductive or more oxidative, depending on the O_2 and CO_2 concentrations in the atmosphere (Cen et al. 2001). The increased O_2/CO_2 ratio is more effective at higher temperatures, providing a higher Rubisco V_o/V_c ratio, and consequently a higher compensation O_2/CO_2 ratio. This is why biological diversity is higher in tropical areas and the spreading of plants occurs from the tropical areas towards moderate and subpolar latitudes (Meyen 1987). In addition, the rate of evolutionary process triggered by an increase in O_2/CO_2 ratio, is mediated by the amount of reactive oxygen species. At higher altitudes, where active oxygen (ozone) is at a high concentration (Sandroni et al. 1994) and UV radiation is strong at lower partial pressures of atmospheric gases, the rate of evolution will be higher. The reduction level in

plants (the flow of reducing power to the synthesis of biomass measured as the reductant utilization rate) strongly depends on the O_2/CO_2 ratio (Cen et al. 2001). Low CO_2 greatly enhances plant stress symptoms (Cowling and Sage 1998), while high CO_2 alleviates these effects. At high O_2 to CO_2 ratios, oxygen can easily be converted to toxic superoxide and hydrogen peroxide, thus causing gene mutations (Raven 1991). An increase in angiosperm biodiversity during the Cenozoic caused for the second time during Phanerozoic, the global long-term depletion of CO_2 in the atmosphere down to the ecological compensation point. The appearance of most C_4 plant species is connected with the late Miocene (8–10 Ma), however in some special areas they appeared earlier and then distributed over the Earth. The C_4 pathway independently evolved over 45 times in 19 families of angiosperms, the earliest likely being in the Chenopodiaceae dating back 15–21 Ma (Sage 2004). The C_4 plants appeared in tropical areas where the compensation ratio is lower, and thus photorespiration is higher. However, C_4 plants had a limited capacity for spreading into colder areas because of the additional energy needed to provide the operation of the C_4 cycle (Sage 2004).

Miocene was characterised by quite low CO_2 concentrations (250–290 ppm) decoupled from temperature (higher by $+6\,°C$ than calculated based solely on the CO_2 concentration), probably because of outbursts of greenhouse methane (Zachos et al. 2001). This high temperature and a high O_2/CO_2 ratio caused a climate favourable for C_4 metabolism. The C_4 plants are adapted to low CO_2 concentrations and warm climate and their photosynthetic metabolism is considered as an efficient CO_2 pump (von Caemmerer and Furbank 2003). They, however, can also prosper at elevated CO_2 concentrations, particularly at elevated temperatures and in arid conditions (Sage and Kubien 2003).

Thus, there is a good indication that the appearance of new genetic material is correlated with periods when the O_2/CO_2 ratio is maximal. During the last million years this was observed during the glaciation periods. Tropical/subtropical areas and mountain regions with a higher degree of oxygen effects were the centres for the origin of cultivated plants (Vavilov 1926). Recessive genes then drifted to the peripheral regions of the species distribution. Cultivated plants are characterised by
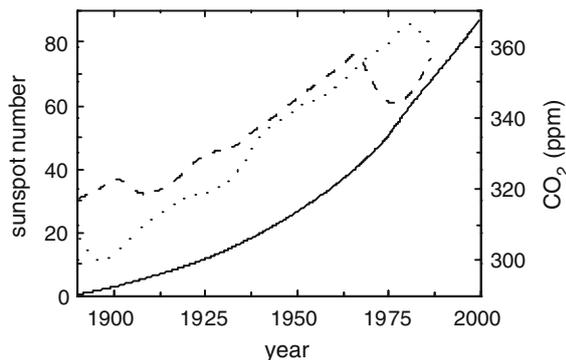
Figure 8. The atmospheric CO_2 concentration (solid line), sunspot number observed (dashed line), sunspot number calculated from [11]Be in Greenland ice (dotted line) during the 20th century. Sunspot data from Usoskin et al. (2003).

a channelling of metabolism towards a higher productivity of certain storage tissues. It is likely that the genetic diversity was built up in tropical areas during glaciation periods, while the spreading occurred during the interglacial periods. Thus the origin of agriculture was linked to the transition from glaciation to higher CO_2 concentrations, when agriculture could be effective.

Greenhouse bursts and their consequences

The rate of increase of CO_2 concentration in the atmosphere was rapid (several-fold in short time periods) on several occasions during Phanerozoic, mostly after impacts of large meteorites (post-apocalyptic greenhouse effects) (Retallack 1999). After these events CO_2 was established at a higher concentration. At the Cretaceous–Palaeogene boundary, there was an increase in CO_2 from 350–500 ppm to 2300 ppm within less than 10,000 years according to the data of stomatal densities (McElwain et al. 1999; Retallack 2001). The CO_2 concentration then decreased to the initial value during hundreds of thousands years (Beerling et al. 2002). The warming impaired leaf photosynthetic function and severely reduced carbon uptake (McElwain et al. 1999). During the Cretaceous–Palaeogene boundary, carbon isotopic recovery (return to the ^{13}C values before the asteroid impact) was observed between $65.00 \pm .05$ Ma and 65.16 ± 0.04 Ma for the terrestrial biosphere (more rapidly than for the marine biosphere), i.e. it took 100–200 thousand years (Ahrens and Jahren 2000; Beerling et al. 2001). This decrease in CO_2 concentration was due to the

unique role of land plants in controlling the O_2 and CO_2 ratio, which is supported by the fact that the terrestrial ecosystems were recovering ahead of marine production (Beerling et al. 2001), however it was relatively slow as compared to the fast greenhouse bursts.

Higher CO_2 concentrations, which persisted for long periods of millions of years, may have resulted either from an unusual solar activity or from the specific properties of the flora with a low weathering rate and slow metabolism (possibly gymnosperms in the Mezozoic). According to the above considerations, we have assumed a major role of photorespiration in maintaining a climate suitable for biospheric development. During the last 1 million years, oscillations of CO_2 concentration near the ecological compensation point were accompanied by corresponding climate changes. They could be explained by a self-regulatory role of the biosphere (a decrease of weathering at the lowest CO_2 concentrations leading to a CO_2 increase), however they were also synchronized with solar activity changes (Rial 2004). The period of these oscillations was around 0.1 Ma and the amplitude was between 180 and 280 ppm, i.e. by about 60% (Sigman and Boyle 2001). Now the indications are that these oscillations will stop, and most scientists claim (Falkowski et al. 2000) that this is due to human activity. However, it is possible that when considering increases in temperature and CO_2, cause and effect may have become confused (Khilyuk and Chilingar 2003).

If we consider the role of the sun in climate change, which during the periods of higher solar activity resulted in an increase in the temperature of the Earth and CO_2 release from oceans to the atmosphere, and even according to some estimates provided about 40% of the present global warming (Beer et al. 2000), we can also attribute the modern increase of temperature and CO_2 to solar activity. The data on sunspot number reconstruction shows that the period of very high solar activity during the last 60 years is unique throughout the last millennium (Usoskin et al. 2003). Taking into account the relatively low CO_2 concentration in the past million years (Royer et al. 2001b) and its oscillations coincident with solar activity, mainly with Milankovitch cycles (cycles in the Earth's orbit that influence the amount of solar radiation including a 100 ka eccentricity cycle corresponding to major glacia-

tions) (Rial 2004), we can regard unusually high solar activity from the middle of the 20th century as an important reason for global warming, which may be comparable to the anthropogenic release of CO_2. It corresponds to the increase of CO_2 occurring exponentially at the present time (Figure 8). A doubling of CO_2 concentration is predicted in 100 years or even less (Falkowski et al. 2000). For such high rate of CO_2 emission, there is no natural process, which can cope with this increase. It is possible that we will return to the Pre-Devonian state, when the CO_2 concentration was high and not fully regulated by the biosphere, and this situation will be beyond human control.

General conclusion

Photorespiration has played an important role since the appearance of land plants, in the regulation of the O_2 and CO_2 concentrations in the atmosphere. The limits of photosynthetic/photorespiratory parameters (O_2/CO_2 compensation ratio) based on Rubisco kinetics, determined limits of variation in O_2 and CO_2 concentrations (O_2/CO_2 ratio). The established atmospheric O_2/CO_2 ratio was coincident with the rates of evolution of land plants. The current increase of CO_2 concentration caused both by anthropogenic burning of fossil fuel and by unusual solar activity is unique, and a similar CO_2 increase did not occur from the early Cenozoic. If we consider the predicted CO_2 increase later than year 2100, the possible effect may be compared even with early Devonian.

Acknowledgements

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