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PHANEROZOIC ATMOSPHERIC OXYGEN

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■ **Abstract** Theoretical calculations, based on both the chemical and isotopic composition of sedimentary rocks, indicate that atmospheric O_2 has varied appreciably over Phanerozoic time, with a notable excursion during the Permo-Carboniferous reaching levels as high as 35% O_2. This agrees with measurements of the carbon isotopic composition of fossil plants together with experiments and calculations on the effect of O_2 on photosynthetic carbon isotope fractionation. The principal cause of the excursion was the rise of large vascular land plants and the consequent increased global burial of organic matter. Higher levels of O_2 are consistent with the presence of Permo-Carboniferous giant insects, and preliminary experiments indicate that insect body size can increase with elevated O_2. Higher O_2 also may have caused more extensive, possibly catastrophic, wildfires. To check this, realistic burning experiments are needed to examine the effects of elevated O_2 on fire behavior.

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INTRODUCTION

The evolution of atmospheric oxygen is intimately intertwined with the evolution of Earth, from both a biological and geological perspective. Much of the attention paid to O_2 evolution has been placed on its rise in the Precambrian and its association with early biological evolution. By contrast, possible changes in atmospheric O_2 since the beginning of the Cambrian have been essentially ignored or assumed to be held to an almost constant level (Watson et al. 1978). It is the purpose of this paper to discuss the factors that both alter and stabilize atmospheric O_2, and to show that the concentration of O_2 could have changed appreciably over Phanerozoic time. We demonstrate that variations of atmospheric O_2 are in accord with the results of geochemical modeling and with studies of the interaction of O_2 with plants and animals. Atmospheric O_2 is controlled principally by the long-term (multimillion-year) geochemical cycles of carbon and sulfur. The effect on O_2 of the cycles of other elements that exhibit variable oxidation states has been shown to be far less significant quantitatively (Holland 1978). The first documented description of how the carbon and sulfur cycles affect O_2 was given by Ebelmen (Ebelmen 1845; see also Berner & Maasch 1996 for a summary) approximately 130 years before independent rediscoveries of the same phenomena by Holland (1978, 1984) and Garrels (Garrels & Perry 1974). Ebelmen deduced the following global reactions:

$$CO_2 + H_2O \leftrightarrow CH_2O + O_2 \tag{1}$$

$$2Fe_2O_3 + 8SO_4^{--} + 16H^+ \leftrightarrow 15O_2 + 4FeS_2 + 8H_2O. \tag{2}$$

Reaction 1, going from left to right, represents net photosynthesis (photosynthesis minus respiration) as represented by the burial of organic matter (CH_2O) in sediments. Going from right to left in Reaction 1 represents two processes: (*a*) the oxidation of old sedimentary organic matter subjected to weathering on the continents and (*b*) the sum of several reactions involving the thermal breakdown of organic matter via diagenesis, metamorphism, and magmatism with the resulting reduced carbon-containing compounds released to Earth's surface where they are oxidized to CO_2 by atmospheric or oceanic O_2.

Reaction 2, going from right to left, represents the oxidation of pyrite during weathering on the continents (reduced organic sulfur is lumped here with pyrite for simplification) and the sum of thermal pyrite decomposition and the oxidation of resulting reduced sulfur-containing gases produced by metamorphism and magmatism. Going from left to right, Reaction 2 is the sum of several reactions. They are (*a*) photosynthesis and initial burial of organic matter (Reaction 1); (*b*) early diagenetic bacterial sulfate reduction and the production of H_2S, with organic matter serving as the reducing agent; and (*c*) the precipitation of pyrite via the reaction of H_2S with Fe_2O_3.

The geochemical sulfur cycle also involves hydrothermal reactions between oceanic crust and seawater sulfate at mid-ocean rises, and these reactions have been advanced as major controls on atmospheric O_2 (Walker 1986, Hansen &

Wallmann 2002). However, there are potential quantitative problems. The flux of water (and therefore of sulfate and sulfide) through mid-ocean rises has been seriously debated (Edmond et al. 1979, Morton & Sleep 1985, Kadko 1996), and the lowest estimates eliminate the hydrothermal reactions as major fluxes in the global sulfur cycle. Also, over 90% of the sulfate removed hydrothermally from the oceans is via $CaSO_4$ deposition (Hansen & Wallmann 2002); this does not involve O_2, and the $CaSO_4$ is later totally redissolved. Oxidation of Fe^{+2} minerals in basalt by hot seawater sulfate results in an irreversible atmospheric oxygen drop over long times (Petsch 1999) and sulfur isotope analyses (Hansen & Wallmann 2002) indicate that over 80% of the H_2S input to seawater at the rises is derived from the mantle (long-term recycling via Reaction 2 going from right to left) and not from seawater sulfate reduction. Finally, the recent work of Rowley (2002) indicates that rates of seafloor crustal production, which should drive the hydrothermal circulation at the rises, may not have changed appreciably over the past 180 million years. This result suggests that changes in the sulfur fluxes at the rises, insofar as they affect oxygen, also may not have changed with time.

The emphasis in this review is on the biogeochemical and surficial aspects of the carbon and sulfur cycles. Most attention is focused on the carbon cycle, which has a considerably greater effect on O_2 than the sulfur cycle. Because of these considerations, and the problems discussed above, there is no further discussion of mid-ocean rise hydrothermal processes.

MODELING THE CARBON AND SULFUR CYCLES AND ATMOSPHERIC O_2

Based on Reactions 1 and 2, a straightforward expression can be written whereby the change of atmospheric oxygen with time can be calculated:

$$dO_2/dt = Fbg - Fwg + 15/8(Fbp - Fwp), \tag{3}$$

where Fbg is the rate of burial of organic carbon in sediments; Fwg is the rate of oxidative weathering of organic carbon plus the rate of oxidation of reduced carbon-containing gases released via diagenesis, metamorphism, and volcanism; Fbp is the rate of pyrite (plus organic) sulfur burial in sediments; Fwp is the rate of oxidative weathering of pyrite (plus organic) sulfur plus the rate of oxidation of reduced sulfur-containing gases released via diagenesis, metamorphism, and volcanism; and the 15/8 term refers to the stoichiometry of Reaction 2. This equation shows that calculation of O_2 over time requires a knowledge of the various fluxes: Fbg, Fwg, Fbp, and Fwp. Estimation of these fluxes has been done by basically two approaches. The “rock abundance” method involves quantifying the amounts of organic carbon and pyrite sulfur in Phanerozoic sedimentary rocks. The other method consists of mass balance calculations based on the carbon and sulfur isotopic composition of the oceans, as recorded in sedimentary rocks.

The rock abundance method (Berner & Canfield 1989) involves estimates of Fbg and Fbp based on (*a*) the average organic carbon and pyrite sulfur concentrations in sedimentary rocks as a function of age and (*b*) original global sedimentation rates. Terrigenous sedimentary rocks (sandstones and shales), where most organic matter and pyrite are found, are divided into three classes: marine sediments; coal basin sediments; and "other" nonmarine sediments, mainly redbeds. The abundances of the three rock types as a function of time are taken from the work of Ronov (1976). Additional assumptions concern the weathering of organic matter and pyrite as affected by stabilization processes. The processes employed by Berner & Canfield are rapid recycling (which involves the compensation of excessive organic matter and pyrite burial by excessive weathering relatively soon after burial) and enhanced C and S weathering accompanying enhanced erosion coupled to enhanced global sedimentation. The results of this rock abundance modeling approach are shown in Figure 1. The prominent Permo-Carboniferous maximum in O_2 is due to increased global rates of burial of organic matter because of a greater contemporaneous abundance of carbon-rich coal-basin sediments. Low O_2 values for the early Mesozoic reflect diminished O_2 production due to global deposition of a high proportion of sediment as organic-free continental redbeds.

The other approach to determine the values of Fbg, Fwg, Fbp, and Fwp over time is through the use of carbon and sulfur isotope data. Variations over Phanerozoic time in $^{13}C/^{12}C$ and $^{34}S/^{32}S$ of the oceans are recorded by the isotopic composition of $CaCO_3$ and $CaSO_4$ in sedimentary rocks (Veizer et al. 1999, Strauss 1999). Changes in oceanic $^{13}C/^{12}C$ largely reflect changes in global photosynthesis, which

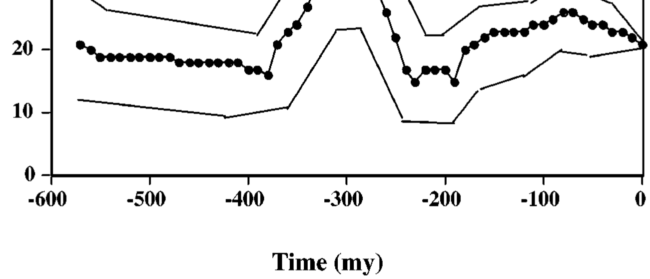

Figure 1 Plot of percent atmospheric O_2 versus time calculated by the rock abundance model. The upper and lower light lines represent the margin of error as deduced by sensitivity analysis (after Berner & Canfield 1989).

brings about the depletion of ^{13}C in sedimentary organic matter relative to the ratio in seawater. Changes in $^{34}S/^{32}S$ largely reflect bacterial sulfate reduction to H_2S, which brings about the depletion of ^{34}S in the resulting sedimentary pyrite. Increased burial of organic matter and pyrite thereby results in greater removal of the lighter isotopes, causing the oceans to become enriched in ^{13}C and ^{34}S. The weathering of organic matter, pyrite, carbonates, and sulfates and the oxidation of reduced gases involve little isotope fractionation. As a result, the composition of the input to the oceans represents a mixture of ^{13}C-depleted carbon and ^{34}S-depleted sulfur from organic matter and pyrite oxidation and ^{13}C-enriched carbon and ^{34}S-enriched sulfur from carbonate and sulfate dissolution.

Rates of weathering, thermal decomposition, and burial of organic matter, pyrite, Ca-Mg carbonates, and Ca sulfates and their changes over Phanerozoic time can be determined by mass balance expressions for total carbon, total sulfur, ^{13}C, and ^{34}S (Holland 1978; Veizer et al. 1980; Berner & Raiswell 1983; Garrels & Lerman 1984; Walker 1986; Kump & Garrels 1986; Francois & Gerard 1986; Berner 1987, 2001; Lasaga 1989; Kump 1989a; Carpenter & Lohmann 1997; Petsch & Berner 1998; Hansen & Wallmann 2002). A representation of this type of modeling is shown in Figure 2. The overall change in the isotopic composition of seawater with time represents the balance between the rates and isotopic

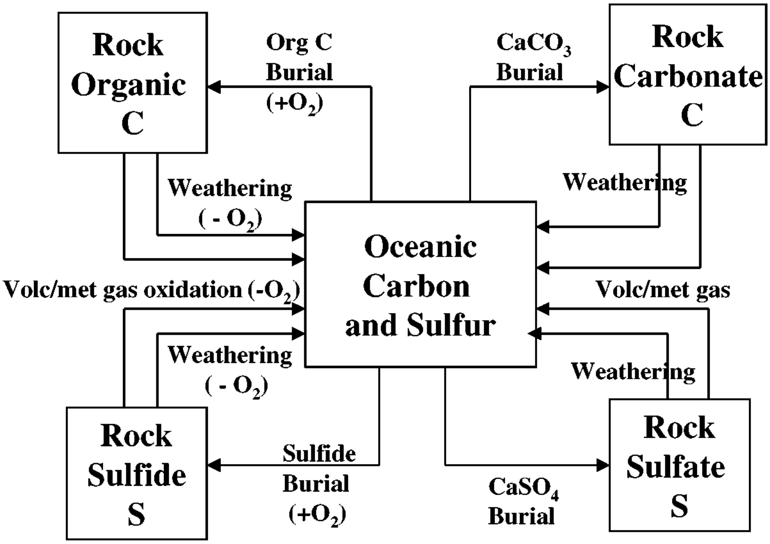

Figure 2 Box model for calculating variations with time in the fluxes affecting atmospheric oxygen. Each box and flux represents both total carbon or sulfur and ^{13}C or ^{34}S. The fluxes for weathering and degassing are often combined under the generalized term "weathering." The symbols ($+O_2$) and ($-O_2$) represent the addition or subtraction of oxygen from the atmosphere.

composition of weathering and thermal degassing inputs and of sediment burial outputs. By starting with present-day rates of weathering, degassing, and burial, past rates can be calculated inversely from the changes in the isotopic composition of the oceans with time. To simplify this calculation, weathering and thermal degassing are lumped together as “weathering” and total crustal carbon and sulfur are assumed to be conserved. As a result, because little carbon can be stored in the ocean, inequalities between weathering and burial of organic matter must result in the reciprocal formation or loss of $CaCO_3$. Sulfur is also conserved by reciprocal behavior of pyrite and $CaSO_4$, although a modest portion of the total sulfur can be stored as dissolved sulfate in the oceans.

Any large difference in the net flux between oxidized and reduced reservoirs of carbon must be eliminated reasonably soon, or be balanced by opposite fluxes between reduced and oxidized reservoirs of sulfur, in order to avoid fluctuations in atmospheric O_2 that would be too large for the maintenance of higher forms of life over geologic time. This leads to the necessity of introducing feedback mechanisms to stabilize O_2 (see next section). The simplest mass balance model (Garrels & Lerman 1984), when applied to both C and S isotopic data using Equation 3, results in fluctuations in O_2 that are physically impossible (i.e., negative mass) because of the great sensitivity of O_2 to the isotopic data (Berner 1987, 2001; Lasaga 1989). The Garrels & Lerman model assumes constant isotope fractionation over time between oceanic carbon and organic matter and between oceanic sulfate and pyrite. To remedy this problem, two mechanisms, which provide feedback but are not normally considered as feedback processes (see next section), have been applied to the model. These are rapid recycling (Berner & Canfield 1989, see above) and O_2-dependent carbon and sulfur isotope fractionation (Berner et al. 2000). Rapid recycling results in a considerable damping of the excessive fluctuations of O_2 but still results in some physically impossible values (Figure 3). Oxygen-dependent isotope fractionation for carbon is based on laboratory photosynthesis experiments (Berner et al. 2000, Beerling et al. 2002) and for sulfur on a reasonable assumption that fractionation during pyrite formation depends on O_2-impacted bioturbation and sediment-water interface recycling. Use of the laboratory results and the sulfur fractionation model results in a calculated curve of O_2 versus time (Figure 3) that damps all excessive O_2 fluctuations and closely mimics predictions based on rock abundance data (compare Figures 1 and 3).

Values for the carbon isotopic fractionation between organic matter and carbonates, calculated by isotope mass balance modeling, agree well with actual measurements of the difference in $^{13}C/^{12}C$ between co-existing organic matter and carbonates (Hayes et al. 1999), especially for the critical Permo-Carboniferous time period. In fact, similar results for O_2 versus time are obtained if the fractionation data of Hayes et al. (1999) for carbon are used in place of the laboratory-determined O_2-dependent values (Berner 2001).

The high Permo-Carboniferous O_2 level of Figure 3, centered around 280 Ma, is the result primarily of unusually high values of $^{13}C/^{12}C$ in the oceans as recorded by carbonate fossils of that age. These high levels are most simply explained

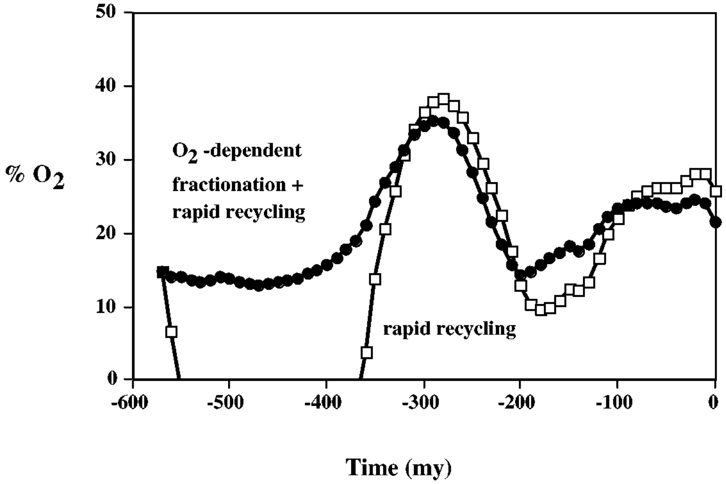

Figure 3 Plot of mass of atmospheric oxygen (in 10^{18} moles) versus time for isotope mass balance modeling. For the definition of rapid recycling, see text. Note the close similarity of the plot for O_2-dependent fractionation to that shown in Figure 1. (Data from Berner 2001.)

by greater burial of organic matter during this period. This is in agreement with the independent reasoning stated above for explaining the results based on rock abundance data. The rise and spread of large vascular land plants in the Devonian led to greater burial of organic matter worldwide. This is because a new source of microbially resistant organic matter, lignin, was created that could be buried both in coal swamps on land and in the oceans after transport there by rivers. (Burial of organic matter on the continents affects the isotopic composition of fresh water and the atmosphere, but because of the flow of rivers to the sea and the rapid isotopic exchange between the atmosphere, surface waters, and the oceans, burial on land is recorded very soon thereafter by a change in the isotopic composition of seawater.) This extra carbon was added to the normal burial of marine, plankton-derived organic matter. The drop in O_2 to low levels during the Triassic is also explained, from this modeling, by a drop in $^{13}C/^{12}C$ and global organic carbon burial due to the virtual disappearance of coal basins, possibly due to changes in sea level and/or in land productivity. The drop could have been considerably more rapid, occurring closer to the Permian/Triassic boundary, due to large-scale deforestation accompanying the Permo-Triassic extinction event (Broecker & Peacock 1999, Berner 2002).

The carbon and sulfur models discussed above are all rather simplified in terms of geological and biological processes. To partly remedy this situation, Hansen & Wallmann (2002) have constructed a comprehensive model that emphasizes tectonics, feedbacks, and their effects on O_2. The GEOCARB model for CO_2 over Phanerozoic time (Berner & Kothavala 2001), which separates volcanic/metamorphic degassing from weathering and considers such things as the uplift of mountains and the rise of land plants as they affect rock weathering, is capable of being augmented to also include O_2. Additional stabilization of O_2 with time would result if oxygen-dependent weathering and/or burial of organic matter were added to the GEOCARB modeling, either directly (Lasaga & Ohmoto 2002) or indirectly via nutrient cycling (Van Cappellen & Ingall 1996, Colman & Holland 2000, Lenton & Watson 2000). However, there is controversy over the quantitative efficacy of these feedback mechanisms, and more work needs to be done before they can be confidently added to the modeling.

FORCINGS AND FEEDBACKS

The level of atmospheric oxygen can be altered (forced) by processes that are geological, biological, or some combination of the two. In the previous section we have mentioned biological forcing by the rise of vascular land plants that brought about an increased global burial of organic matter. In this section, we try to distinguish geological (tectonic) forcing from biological forcing, but with an understanding that discrimination between the two is often not possible. For example, uplift of mountains (tectonics) favors the weathering of phosphate minerals that supply nutrients to the oceans for use in organic matter production and burial. However, the rate of weathering of the phosphates can be strongly impacted by the nature of the montane vegetation.

Inseparably entwined with forcings are feedbacks. There have been many suggested feedback mechanisms that might stabilize atmospheric oxygen, and the primary purpose of this section is to discuss a number of them. To present this discussion in a succinct manner, we have turned to the use of systems analysis diagrams as already employed by others (e.g., Kump 1988, Berner 1999, Lenton & Watson 2000). In these diagrams (Figures 4–7) plain arrows with no attached "bullseyes" represent a direct response. In other words, if a certain quantity increases, a plain arrow means that the quantity or process at the end of the arrow also increases. An arrow with an attached bullseye represents an inverse response. In this case, if the source of the arrow increases, the quantity at the end of the arrow decreases. By following arrows around various loops, one can immediately discern whether the overall process results in positive feedback or negative feedback. If the sum of bullseyes is even or zero, there is net positive feedback. If the sum of bullseyes is odd, there is negative feedback. For the sake of brevity, all discussions of the diagrams are in terms of an initial rise in the level of atmospheric O_2.

C-S–O_2 Diagram

To introduce the use of systems diagrams we present Figure 4. Here, the major processes discussed in the previous modeling section are shown along with feedback loops. The arrows leading to and from O_2 represent suggested simple feedbacks. However, there is considerable disagreement about those represented by dashed lines. This is because it is believed that there are other factors, such as the enhancement of organic weathering by erosive stripping and organic burial by total sedimentation, that dominate over the direct effects of O_2 on these processes (Holland 1978, 1984). By contrast, Lasaga & Ohmoto (2002) have recently emphasized the importance of the dashed arrows as providing stability to atmospheric oxygen. Note that the loops between O_2 and the weathering and burial of organic matter and pyrite all result in negative feedback. Lasaga & Ohmoto believe that these simple feedbacks dominate over those involving more indirect controls on stability, such as weathering, erosion, and nutrient cycling.

The plain arrows around the exterior of Figure 4 represent additional phenomena not usually covered in discussions of O_2 stability. The top and bottom arrows leading from burial to weathering simply mean that greater burial of organic matter and pyrite can lead to greater weathering at a later date when the buried rocks are uplifted onto the continents and are exposed to erosion and weathering. This can lead to a special kind of non-loop negative feedback, as can be seen, for example, by following the paths: organic C burial → organic C weathering → O_2 combined with organic C burial → O_2. The effect of greater burial of organic matter on increasing O_2 is counterbalanced later by the greater weathering of the same uplifted organic matter. This process, if the time between burial and weathering is sufficiently short, can lead to negative feedback and is termed rapid recycling (Berner & Canfield 1989), which is discussed in the previous section on modeling.

In most fine-grained marine sediments, pyrite (FeS_2) positively correlates with organic matter (Berner & Raiswell 1983), as shown by the upward-directed arrow on the left end of the diagram. Thus, greater O_2 production by greater organic C burial should result in even more O_2 production by greater pyrite S burial. The downward-directed arrow at the right end of the diagram leading from FeS_2 weathering to organic C weathering illustrates a direct response that should be considered in any study of the weathering of organic matter (Petsch et al. 2000). Pyrite oxidation during weathering leads to the formation of H_2SO_4, which can readily attack silicate and carbonate minerals that protect or occlude organic matter. Dissolving and disintegrating the minerals, as a result of pyrite weathering, thereby helps to expose the organic matter itself to oxidative weathering.

Geological Forcing

Geological forcing of O_2 is presented here separately because it is often ignored by some proponents of the biologically oriented Gaia hypothesis (Lovelock 1988). Figure 5 presents a selection, by no means complete, of some geological forcings. (The feedback loops discussed in the preceding section between weathering, burial, and O_2 are also included in Figure 5 for the sake of completeness.) Geological forcings are considered "external," in other words, not part of a feedback loop; they are continental relief and volcanic-metamorphic-diagenetic release of reduced gases (e.g., SO_2, CH_4, H_2S). Decrease in O_2 via the oxidation of reduced gases (*arrow g*) is an inverse response to increased degassing. Increased continental relief and glaciation result from mountain building and entail enhanced erosion (Milliman & Syvitski 1992). All arrows leading from continental relief are plain without bullseyes, indicating that increased erosion results in increased chemical weathering due to the removal of overburden that protects primary minerals from dissolution (e.g., Stallard 1985, Gaillardet et al. 1999). The influence of uplift, relief, and weathering on atmospheric O_2 has been discussed by Holland (1978) and Lasaga & Ohmoto (2002). The effect on phosphate weathering is especially important in that phosphate is an essential nutrient in the production of organic matter and, ultimately, in its burial (*arrow f*). Increased erosion also leads, by necessity, to increased sedimentation, and increased total sedimentation involves the greater burial of organic matter (*arrow a*) and pyrite (*arrow b*) (Holland 1978, Berner & Canfield 1989, Des Marais et al. 1992).

Nutrient Cycles and O_2

There have been a number of hypotheses concerning the control of atmospheric O_2 by the biogeochemical cycling of nutrient elements, specifically phosphorus and nitrogen. Figure 6 illustrates some of these suggested controls. Colman & Holland (2000) and Van Cappellen & Ingall (1996) emphasize a negative feedback loop that assumes that phosphorus limits marine plankton production on a geological timescale. Their idea is represented by the path k – p – n – j, which has one arrow with a bullseye. An increase in atmospheric O_2 results in increased dissolved oxygen levels of the oceans and a greater sedimentary burial of ferric oxides associated with adsorbed phosphate (FeP). This enhanced FeP burial results in a lowering of the level of dissolved phosphate (aqueous P) available for photosynthetic plankton production. Less production results in less sedimentation and burial of organic matter and, thus, less O_2 production. In this way, there is an overall negative feedback against a change in atmospheric O_2.

A more involved negative feedback, championed by Lenton & Watson (2000), is represented by the path f – b – a – n – j, which again has just one arrow with a bullseye. High levels of O_2 adversely affect land plants (by causing fires and photorespiration); thus, increases in O_2 diminish the standing crop of plants. Fewer plants mean fewer roots working the soil and less weathering of phosphate minerals. Less phosphate weathering should then lead to a lower input of dissolved P to the oceans, lower levels of oceanic aqueous P, less organic production, less organic burial, and finally, less O_2 production. However, because ecosystems often respond to fire by increases in the root/shoot ratio, increased root mass could mitigate the effects of the thinning of vegetation with more fires.

Falkowski (1997) has argued that, on a geological timescale, the limiting nutrient for planktonic production is nitrogen, not phosphorus. A negative feedback loop would be g – i – j. Increased O_2 inhibits the fixation of N_2, which in turn inhibits the planktonic production of organic matter and the production of O_2 by means of its burial. However, recent studies (Sanudo-Wilhelmy et al. 2001) have shown that nitrogen fixation in areas of the subtropical Pacific ocean is limited by phosphorus availability. This makes P the limiting nutrient and gives rise to the arrow (*m*) between nutrient aqueous P and N fixation. In this case, a negative feedback loop could be k – p – m – i – j.

Another possible feedback apparent from examination of Figure 6, not considered by others, is f – c – d. This is a positive feedback loop, but it depends on the assumption that plant root activity accelerates the weathering of sedimentary organic matter, as well as phosphate minerals. Finally, there are the simple negative feedbacks, e – d and h – j, emphasized by Lasaga & Ohmoto (2002) and not involving P or N that have been discussed earlier.

Fires and Feedback

Oxygen stimulates fire. Fire, in turn, causes rapid breakdown of organic material and major changes in ecosystem form and function. The resulting interaction of oxygen, fires, and biota potentially results in multiple feedbacks (Figure 7). Consider the path b – c – j – g. A rise in O_2 should bring about an increase in fires, which should, in turn, cause a decrease in land biomass. This should lead to less organic matter burial, less O_2 production, and, thus, negative feedback. (For the sake of completeness, the deleterious effect of O_2 on plants via photorespiration is shown by the shorter cycle f – j – g, which is another negative feedback mechanism.)

However, fires can also lead to positive feedback with regard to atmospheric oxygen. An example is the formation of charcoal. Charcoal is much more resistant to biological decomposition than is plant biomass; thus, charring of decomposable plant biomass leads to enhanced organic matter preservation. If O_2 rises and more charcoal is produced by fires, then there is more organic carbon burial and increased O_2 production. This is positive feedback represented by the path b – a – i – g. The charcoal feedback may be reinforced by evolutionary responses to fire. The promotion of char formation is an effective fire retardant, and plants under selective pressure from fire could be expected to produce tissues rich in compounds, such as lignins and tannins, that promote charring and retard fire. This would doubly reinforce the positive feedback in b – a – i – g, first by increasing the charcoal yield from burning, and second because chemical properties such as condensed bonds that enhance char formation also tend to retard biological decay by increasing the fraction of unburned organic matter that is preserved in the sediments.

Land plants also hold soil against erosion. Their destruction by fire leads to enhanced erosion and more transport of soil material to the sea. This greater erosion brings about greater marine sedimentation, which in turn brings about greater burial of organic matter and enhanced O_2 production. The path b – c – d – e – g contains two arrows with bullseyes and thus is another positive feedback. These positive feedbacks emphasize that increases in atmospheric O_2 and fires do not necessarily lead to negative feedback.

Kump (1988) and Lenton & Watson (2000) have emphasized fire as a negative feedback mechanism by perturbing the phosphorus cycle. Lenton & Watson favor a feedback mechanism, which has already been discussed in the section on nutrients, whereby fires reduce plant biomass and lessen the release of phosphorus by plant-assisted chemical weathering. The Kump model involves the loss of phosphorus to the sea by reduced uptake via land plants due to fire. The C/P ratio of land plants is much higher than that of marine plankton. As a result, the loss of P to the sea would produce less carbon per mole of organic P buried than if the P were being buried in terrestrial organic matter. In this way, for a given amount of global phosphorus burial, fire brings about lower organic burial and less O_2 production, providing negative feedback to any rise of O_2.

O_2 AND PLANTS

Photosynthesis and Carbon Isotope Discrimination

Changes in the concentration of atmospheric O_2 exert a direct influence on a range of leaf gas exchange processes in C_3 plants, especially photosynthesis and photorespiration, with consequences for plant growth (Raven et al. 1994, Raven 1991). These processes, in turn, influence the carbon isotopic composition of plant materials and, ultimately, that of fossilized terrestrial organic carbon. In theory at least, therefore, modeled fluctuations in atmospheric O_2 levels should imprint a shift in the carbon isotopic composition of fossil plants. This theoretical expectation has been confirmed by results from controlled environment plant growth experiments showing that isotopic fractionation is sensitive to atmospheric O_2 (Berner et al. 2000, Beerling et al. 2002).

It is important to assess, however, how other features of the plant growth environment, specifically temperature and the level of atmospheric CO_2, may influence the effect of O_2 on the isotopic response of plants. In the absence of more detailed experiments, this can be achieved by theoretical analyses of leaf gas exchange behavior. A modified version of a coupled mathematical model describing the integrated functioning of photosynthesis and stomatal conductance has been used here to achieve this aim (Farquhar & Wong 1984). Experimental observations suggest that stomatal conductance to water vapor either shows no change with increasing O_2 content (Farquhar & Wong 1984) or, more typically, increases (Rachmilevitch et al. 1999, Gale et al. 2001). The Farquhar & Wong (1984) model fails to simulate both a rise in conductance with O_2 and its attenuation with a rising background CO_2 level. Therefore, to investigate the consequences of this response mathematically, an empirical multiplier (*mult*) is derived, approximately fitted to experimental data (Rachmilevitch et al. 1999, Gale et al. 2001) and given by:

$$mult = 0.5687\,\exp[-0.0005\,[CO_2 \times 10] + 0.0476\,[O_2]], \tag{4}$$

where $[CO_2]$ and $[O_2]$ are the concentrations of atmospheric CO_2 (ppmv) and O_2

(%), respectively. Equation A17 of Farquhar & Wong (1984), which describes stomatal conductance (g_s, mol m^{-2} s^{-1}), is then given by:

$$g_s = 10^5 \mathrm{p}\,\mathrm{T}\,mult, \tag{5}$$

where p is the areal density of chlorophyll (500×10^{-6} mol m^{-2}) and T is a parameter generally related to the ATP content per unit leaf area (mol m^{-2}) of the mesophyll chloroplasts.

We used this modified version of the Farquhar & Wong (1984) gas exchange model to investigate the possible effects of temperature and atmospheric CO_2 levels on leaf gas responses to atmospheric O_2 and assess the likely magnitude of shifts in leaf carbon isotope discrimination. Carbon isotope discrimination by leaves (Δ) was calculated from the equilibrium values of intercellular to atmospheric CO_2 concentration (c_i/c_a) from the gas exchange models according to the well-validated model (Farquhar et al. 1982) given by:

$$\Delta = a + (b - a)c_i/c_a, \tag{6}$$

where a is the fractionation that occurs during diffusion through the stomata (4.4 ‰) and b is the kinetic fractionation that occurs during the fixation of CO_2 by Rubisco (27‰–29‰).

We first consider how gas exchange responses to atmospheric O_2 are modified by atmospheric CO_2 at a constant temperature. The simulations indicate that a rising atmospheric O_2 content reduces rates of leaf photosynthesis, but to an extent that is diminished at higher background levels of CO_2 (Figure 8), due to CO_2 competitively inhibiting the oxygenase reaction of Rubisco and, thereby, suppressing photorespiration (Lawlor 2001). Because of this effect, as O_2 rises the photosynthetic draw-down of CO_2 within the sub-stomatal cavities of leaves decreases. Together with a corresponding rise in leaf conductance, this allows the c_i/c_a ratio to increase and Δ values to rise (Equation 6) (Figure 8). At any given O_2 concentration, the effect of a 200 ppmv increase in CO_2 on Δ is modeled to be much less than that of a rise in O_2 between 20% and 35% (Figure 8).

Temperature can also modify how leaves respond to O_2 by altering the relative solubilities of CO_2 and O_2, the specificity of Rubisco for CO_2, and the degree of stomatal closure due to changes in relative humidity (Lawlor 1993). A further set of simulations investigating the effect of temperature, but at a constant CO_2 concentration, is presented in Figure 8. As with variable CO_2, for variable temperature, photosynthetic rates decline with increasing O_2 with similar effects on leaf Δ values. Similar results for the effects of temperature and CO_2 were obtained using an unmodified stomatal conductance response in the Farquhar & Wong (1984) model.

To check on the modeled responses of leaf Δ to O_2, the results were tested by recalculating them as the change in discrimination at some altered O_2 level relative to 21%, given by:

$$\Delta(\Delta) = \Delta(\text{at altered } O_2 \text{ level}) - \Delta\ (\text{at } 21\%\ O_2), \tag{7}$$

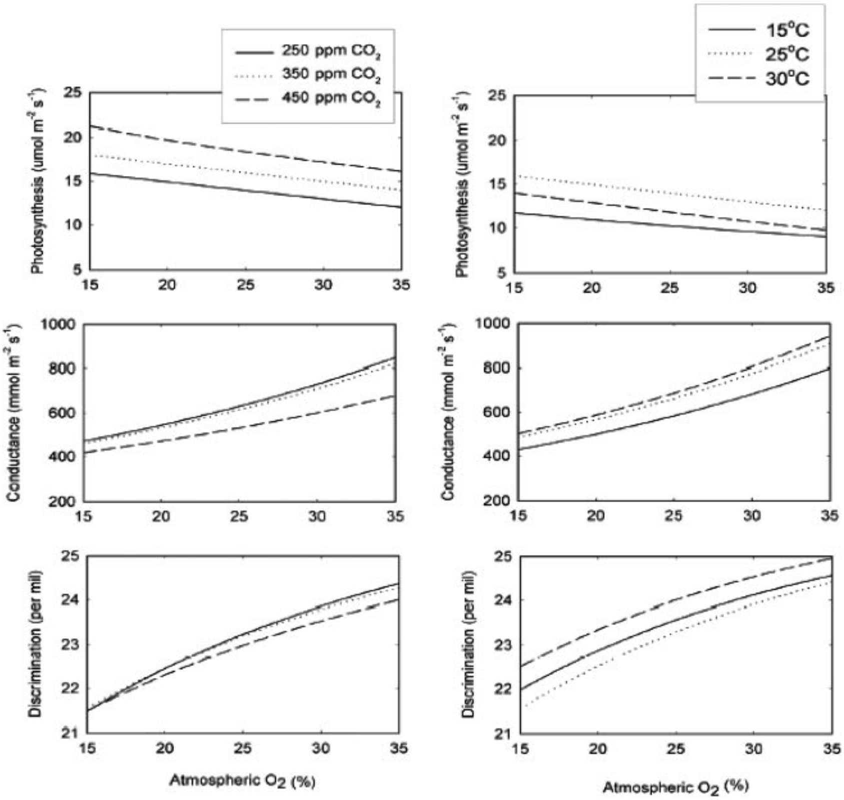

Figure 8 Modeled responses of leaf photosynthesis, stomatal conductance, and carbon isotope discrimination to changes in atmospheric O_2. The left-hand panels show the effect of a varying background level of atmospheric CO_2 at a constant temperature (25°C); the right-hand panels show the effect of temperature at a constant atmospheric CO_2 concentration (300 ppm). All simulations were made at an irradiance of 1500 μmol m^2 s^{-1} and with maximum rates of carboxylation (V_{max}) and electron transport (J_{max}) of 100 and 161 μmol m^{-2} s^{-1}, respectively.

to facilitate comparison with observations from O_2 experiments summarized by Beerling et al. (2002). The comparison reveals that the magnitude and direction of the modeled change in Δ are both in reasonable agreement with observations (Figure 9).

Overall, both the experimental evidence and model simulations of leaf gas exchange consistently indicate that an increase in atmospheric O_2, as predicted during the Permo-Carboniferous, would increase isotopic fractionation by vascular land plants. The response is mediated by an O_2-induced drop in photosynthesis causing the c_i/c_a ratio to rise. These results, and those of an independent theoretical

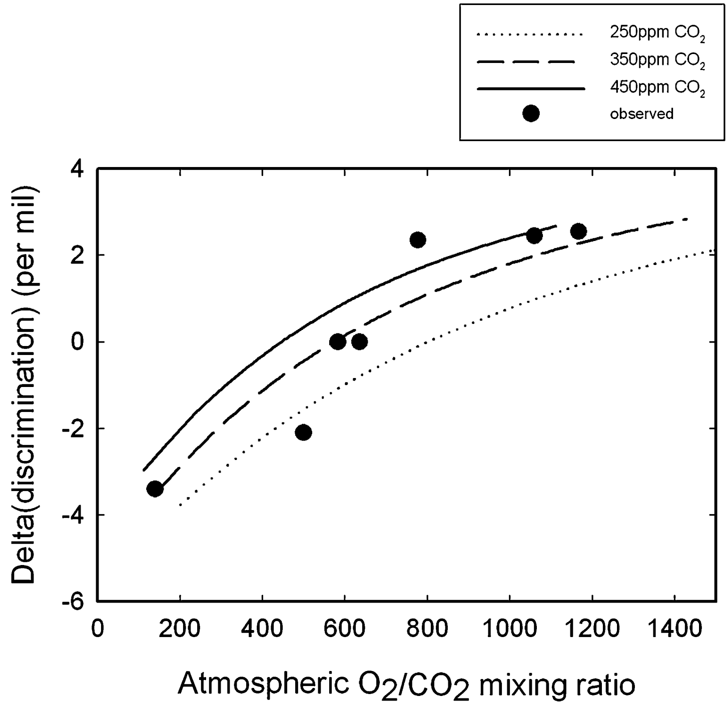

Figure 9 Calculated changes in carbon isotope discrimination from current conditions [delta (discrimination) = 0] in response to varying atmospheric O_2/CO_2 ratios compared with observed changes from laboratory growth experiments. Observations from Beerling et al. (2002).

treatment (Beerling & Woodward 2001), point to the potential for detecting a positive excursion in the isotopic fractionation of Late Paleozoic fossil plant carbon, if atmospheric O_2 levels rose to around 35%.

Beerling et al. (2002) report isotopic analyses and calculation of plant fractionation for fossil plants between the Devonian and the Triassic. The results (Figure 10) show an excursion in $\Delta^{13}C$ values consistent with a major O_2 excursion predicted by the isotope mass balance geochemical model. However, there is some uncertainty in the global signal of the isotopic composition of atmospheric CO_2 required for calculating plant Δ values, when determined from the marine carbonate record, because the records for the Permo-Carboniferous differ (Veizer et al. 1999, Mii et al. 1999).

Atmospheric O_2 and Productivity of the Terrestrial Biosphere

Global-scale simulations with a process-based terrestrial carbon cycle model and a Carboniferous climate, simulated with the U.K. Universities Global Atmospheric

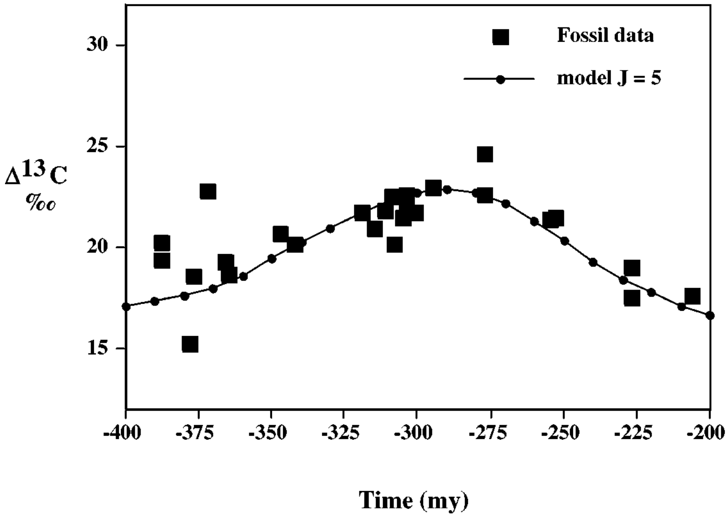

Figure 10 Plot of carbon isotope discrimination between atmospheric CO_2 and plant organic matter ($\Delta^{13}C$) as a function of time for the Devonian-Triassic. Plotted squares represent discrimination based on measurements of bulk plant fossil carbon combined with estimates of the $\delta^{13}C$ of contemporaneous air derived from marine carbonate $\delta^{13}C$ values (data from Beerling et al. 2002). The line with small points is based on the carbon isotope model of Berner (2001), with $J = 5$, where discrimination is assumed to be dependent on atmospheric O_2 level and to follow the expression $\Delta^{13}C = \Delta^{13}C(0) + J[O_2(t)/38 - 1]$, where $\Delta^{13}C(0)$ is the $\Delta^{13}C$ value for the present level of O_2, $O_2(t)$ is the mass of oxygen in the atmosphere at time t, 38 is the mass of oxygen in the present atmosphere (in 10^{18} moles), and J is the adjustable curve-fit parameter.

Modelling Programme general circulation model (Beerling et al. 1998), show quite clearly that an O_2 pulse to 35% could have curtailed net primary production by around 20% (Beerling & Berner 2000). The effects of climate and attenuating influence of the background atmospheric CO_2 level impact directly on this figure of 20%, indicating that the leaf-level issues considered earlier scale up to the entire terrestrial biosphere.

Cyclical Permo-Carboniferous sea level fluctuations have long been linked to Milankovitch-type orbital forcing (Crowley et al. 1993). Therefore, changes in climate caused by Milankovitch variations in insolation during the Carboniferous represent a further potentially important interaction between the terrestrial carbon cycle, climate, and the chemical composition of the atmosphere. Furthermore, if atmospheric CO_2 levels varied between glacial and interglacial values during times of high O_2, then major changes in terrestrial carbon storage probably ensued.

A series of terrestrial carbon simulations dealing with these issues have been performed (D.J. Beerling & B. Otto-Bliesner, manuscript in preparation). This study used Carboniferous climate simulations made with the U.S. National Center for Atmospheric Research climate model, configured with either a cold or hot summer orbit, and a terrestrial carbon cycle model (D.J. Beerling & B. Otto-Bliesner, manuscript in preparation). It emerges that an increase in O_2 from 24% to 35% during the Carboniferous would reduce global net primary production of the terrestrial biosphere by 10% irrespective of interglacial-glacial climate state (Table 1).

A 10% drop in productivity due to high O_2 levels is approximately the same magnitude as that modeled to occur with a switch from a warm to a cool summer orbit climate.

If, however, these changes in climate were accompanied by fluctuations between glacial (180 ppm) and interglacial (300 ppm) CO_2 levels, by analogy with ice core records of Quaternary glacial cycles, then the simulations indicate the terrestrial biosphere would have played an important role in sequestering and releasing several hundred gigatonnes of carbon from the atmospheric pool (Table 1).

TABLE 1 Effects of O_2 and glacial-interglacial CO_2 fluctuations on global terrestrial net primary productivity (NPP) and carbon storage during the Carboniferous

	Glacial climate[a] O_2 concentration		**Interglacial climate[b] O_2 concentration**	
	24%	**35%**	**24%**	**35%**
Effects of climate and atmospheric O_2 at 300 ppm CO_2				
NPP (Gt C $year^{-1}$)	53	46	61	52
Carbon storage in vegetation biomass (Gt C)	740	591	876	701
Carbon storage in soil organic matter (Gt C)	1488	1408	1513	1416
Total biospheric C storage	**2228**	**1999**	**2389**	**2117**
	Glacial climate $CO_2 = 180$ ppm O_2 concentration		**Interglacial climate $CO_2 = 300$ ppm O_2 concentration**	
	24%	**35%**	**24%**	**35%**
Effects of climate, atmospheric O_2 and CO_2				
NPP (Gt C $year^{-1}$)	36	28	61	52
Carbon storage in vegetation biomass (Gt C)	393	244	876	701
Carbon storage in soil organic matter (Gt C)	1266	1143	1513	1416
Total biospheric C storage	**1659**	**1387**	**2389**	**2117**

[a] Climate derived with a "cool" summer orbital obliquity of 21°.

[b] Climate derived with a "hot" summer orbital obliquity of 24°.

At a glacial low CO_2 concentration, productivity of the terrestrial biosphere becomes more sensitive to high O_2 levels, dropping by 22% (Table 1). The interaction between terrestrial vegetation and global atmospheric CO_2 levels, as well as its influence on the hydrological cycle (Beerling & Berner 2000), and the exchange of energy and materials represents an area poorly quantified for the Carboniferous but in urgent need of further research.

O_2 AND ANIMALS

Changes in atmospheric oxygen levels impinge on diverse features of animal physiology. Thermal balance, respiratory gas exchange, and the aerodynamics of animal flight are but some of the physiological and biomechanical phenomena influenced by a variably oxygenated atmosphere. For terrestrial and aerial organisms, a broad range of gaseous physical parameters must be considered, including air density, viscosity, specific heat, thermal conductivity, and the diffusivity of oxygen (Graham et al. 1995, Dudley & Chai 1996, Gans et al. 1999, Dudley 2000). In water, variable coupling of oxygen levels to that in air indicates that oxygenation of aquatic systems will not perfectly track atmospheric composition, although some biological effects may still be expected. In both water and air, however, the dramatic atmospheric changes of the late Paleozoic would have substantially impinged on the physiology of contemporaneous taxa. Zoological bioindicators of atmospheric composition (in both air and water) are most likely to be found in the Carboniferous and Permian.

From an evolutionary perspective, the hypothetical rise in late Paleozoic oxygen levels must be viewed as a slow and persistent drift in environmental conditions rather than as an immediate selective force. Predicted rates of increase in atmospheric oxygen were sufficiently low during the rise (e.g., $<1\%/\mathrm{Ma}$) as to permit gradual genetically based phenotypic responses (i.e., evolution). The drop in O_2 after the maximum may have been similarly gradual (Figure 3), but recent work suggests that it could have been abrupt at the Permian-Triassic boundary (Berner 2002). In the latter case, this would have been due to a rapid reorganization of the global carbon and sulfur cycles (Broecker & Peacock 1999) accompanying the catastrophic biological extinction that occurred at this time. The partial pressure of oxygen associated with the 15% atmospheric content predicted for the early Triassic corresponds to a contemporary partial pressure of this gas at an altitude of approximately 2.5 km. Virtually all extant animal taxa readily tolerate such moderate hypoxia (Bouverot 1985, Mangum 1997). Because Phanerozoic hyper- and hypoxia involved changes in oxygen concentration as well as in atmospheric density, these conditions differ from those obtained experimentally in a hyper- or hypobaric chamber, within which the oxygen concentration remains constant but total pressure is changed. Nonetheless, experimental variation in total pressure using today's air is a convenient and physiologically conservative proxy (see below) for simulating historical change in the availability of atmospheric oxygen. This is because at constant oxygen concentration, any fractional increase in total pressure is matched by an equivalent increase in oxygen partial pressure, the latter being of major physiological importance.

Oxygen availability in water, a function of both gaseous partial pressure and its temperature-dependent solubility, constrains body size in aquatic invertebrates (Graham 1990, Chapelle & Peck 1999, Spicer & Gaston 1999). The maximum radius for a diffusion-limited spherical organism (i.e., the Krogh radius) varies in direct proportion to the square root of the oxygen partial pressure at the surface of the organism; this radius in either air or water increases by approximately 27% for the upper-level estimate of late Paleozoic oxygen values (Graham et al. 1995). Enhanced oxygenation of freshwater ecosystems would have broadened life history possibilities for various aquatic arthropods, including the larval stages then evolving in many basal insect lineages (e.g., Ephemeroptera, Odonata, Plecoptera; see Wootton 1988, Dudley 2000). In the oceans today, many benthic invertebrate taxa attain maximum diversity at oxygen-stressed depths and compensate for hypoxic conditions via a broad spectrum of behavioral and morphological adaptations (Rogers 2000). Infaunal penetration is the most straightforward of such responses to enhanced sediment oxygenation, but greater mobility and broadening of temporal activity patterns are equally plausible outcomes. Variable oceanic oxygenation derived from atmospheric fluctuations would likely have induced corresponding evolution in depth-dependent mechanisms both to tolerate hypoxia and to take advantage of hyperoxia. Increasing atmospheric oxygen levels have, for example, been implicated in the rise of late pre-Cambrian and Cambrian marine faunas (Cloud 1976; Runnegar 1982a,b; McMenamin & McMenamin 1990; Gilbert 1996). Similarly, anoxia has been regularly correlated with the dramatic Permo-Triassic extinction events in the ocean, although multiple factors have been implicated in this phenomenon (Hallam 1991, Erwin 1993, Knoll et al. 1996, Wignall & Twitchett 1996). End-Permian extinctions may have been particularly rapid both in the ocean and on land (Jin et al. 2000, Smith & Ward 2001), prompting the suggestion that rapid change in atmospheric composition was a substantial contributor to these events (Berner 2002).

Terrestrialization by plants yielded an increasingly arborescent vegetation through the Devonian and Carboniferous. Terrestrial plants, in turn, provided abundant physical and nutritional substrates for the evolution of associated animal communities. For example, climbing of trees characterized some Carboniferous horseshoe crabs that must otherwise have remained immersed to effect gas exchange via book gills (Fisher 1979). Gliding scenarios for flight evolution by insects in either the Upper Devonian or Lower Carboniferous presuppose three-dimensional climbing and evasive startle jumps within vegetation (Flower 1964, Ellington 1991, Wootton & Ellington 1991, Kingsolver & Koehl 1994). Any of the various existing scenarios for insect flight evolution, however, would advantageously incorporate a hyperoxic and correspondingly hyperdense atmosphere (Dudley 2000). Increased air densities yield greater aerodynamic forces as well as higher Reynolds numbers advantageous for lift production by winglets or protowings, whereas oxidative flight metabolism would be enhanced by greater gaseous flux within the diffusion-limited respiratory system of insects (Vogel 1994, Dudley 2000). Subsequent to origins of flight and parallel with the increasing complexity of terrestrial plant communities, feeding morphologies of phytophagous insects diversified substantially in the Carboniferous and Permian (Wootton 1990, Shear 1991, Labandeira 1998).

The most obvious zoological support for a postulated late Paleozoic rise in oxygen, however, is the contemporaneous expression of gigantism within numerous unrelated arthropod lineages (Briggs 1985; Kukalová-Peck 1985, 1987; Shear & Kukalová-Peck 1990; Graham et al. 1995). All insects, and more generally many arthropods, use arborized tracheal networks to effect respiration. Tracheal arborizations, particularly in terminal tracheoles, are diffusion-limited and impose an upper limit to insect thoracic dimensions given the intense metabolic demands of active flight muscle (Weis-Fogh 1964a,b; Mill 1985). Relaxation of this physiological constraint by atmospheric hyperoxia in the late Paleozoic thus would have permitted the evolution of increased body size in such taxa; all such giant arthropods subsequently went extinct by the late Permian, exactly as would be predicted by their respiratory asphyxiation on a global scale due to decreasing atmospheric O_2 (Graham et al. 1995, Dudley 1998).

Given the potential implications of variable oxygen levels for insect evolution, it is surprising how little is known about the effects of enhanced oxygen availability on insects (as opposed to hypoxia resistance and ontogenetic tracheal hypertrophy; Loudon 1988, 1989; Greenberg & Ar 1996; Holter & Spangenberg 1997; Greenlee & Harrison 1998). Recent studies, however, illustrate the potential consequences of hyperoxia for both larval development and adult locomotor physiology. Harrison & Lighton (1998) demonstrated a linear relationship between oxygen availability and flight metabolic rates in a free-flying dragonfly species, a result consistent with diffusion-based restrictions on thoracic oxygen flux. On a much longer timescale, growth experiments with the fruitfly *Drosophila melanogaster* in conditions of variable oxygen availability yielded an increased growth rate and greater adult body mass under hyperoxia, although some gender differences in response were also apparent (Frazier et al. 2001). These increases occurred relative to both hypoxia and normoxia, but were also temperature-dependent, with reduced effects at lower temperatures apparently deriving from a concomitant reduction in the oxygen diffusion coefficient as well as in oxygen solubility in water (Frazier et al. 2001). Moreover, the hyperoxic treatment used in these experiments was carried out with a normobaric gas mixture of 40% O_2/60% N_2. The associated partial pressure of oxygen lies outside of the likely historical range for the atmosphere (Berner & Canfield 1989, Berner 2001), and may be sufficiently high as to exert toxic effects (Kloek et al. 1976, Baret et al. 1994, Shigenaga et al. 1994).

Ongoing hyperbaric manipulations using the fruitfly genus *Drosophila* (R. Dudley, unpublished data) further illustrate the wide-ranging influence of oxygen availability on insect biology. Hyperbaria imperfectly simulates hyperoxic conditions of the late Paleozoic, during which time both oxygen concentration and partial pressure of this gas are believed to have increased. However, an increase in

TABLE 2 Gender (sample size *N*) and mean values (standard deviation) of wet body mass for a control line of *Drosophila melanogaster* (Oregon strain) and an experimental line chronically exposed to hyperbaria over five generations

Treatment	Gender	Body mass (mg)
normobaria	female (32)	1.07 (0.19)
	male (30)	0.64 (0.07)
hyperbaria	female (31)	1.18 (0.24)
	male (36)	0.73 (0.12)

Table data refer to adult body mass of a sixth generation for each line raised under equivalent normobaric conditions in order to exclude intragenerational effects of phenotypically plastic responses to hyperbaria. Experimental and control lines were maintained in cylindrical Nalgene chambers (6.5-cm radius × 20-cm height) within an environmental room held at 28.0°C. Relative humidity of air within both experimental and control chambers was maintained near 100%. Air pressure within the experimental chamber was increased using a single-head diaphragm pump (Air Cadet). Pressures were monitored daily over 50 days in the hyperbaric treatment (mean: 1.101 atm, s.d: 0.007 atm) and in the normobaric control (mean: 1.003 atm, s.d: 0.009 atm). Partial pressures of oxygen under hyperbaric and normobaric conditions averaged 0.23 atm (174.9 mm Hg) and 0.21 atm (159.3 mm Hg), respectively. Larval growth medium was provided in a Petri dish at the base of each chamber, and was replaced every 10 days. See text for statistical results.

both total pressure and oxygen partial pressure has the advantage of maintaining a constant diffusive flux of oxygen in air because of the concomitant pressure-dependent reduction in the gaseous diffusion coefficient (Reid et al. 1987). Results of some initial experiments are shown in Table 2. Body masses in *Drosophila* following five generations of growth in chronic hyperbaria increased significantly over those for a normobaric control population with analysis of variance between groups (ANOVA), $F = 19.1$, $P < 0.0001$. Using mass data determined at each generation and for each sex, females were found to be significantly heavier than males ($F = 30.9$, $P < 0.0001$), and body mass increased significantly with generation number ($F = 13.3$, $P < 0.001$). Potential statistical interactions among treatment, generation number, and gender were all non-significant, with the exception of a significantly negative treatment-by-generation interaction ($F = 12.7$, $P < 0.001$), indicating a reduced response to hyperbaria at subsequent generations. Reduced response would be expected for acclimatization to an elevated O_2 level.

An equivalent experiment, but over only a single generation using a substantially higher air pressure (1.196 atm with $pO_2 = 0.25$ atm) failed to show differences in body mass between controls and experimentals for either gender. Frazier et al. (2001) similarly found over a single generation no effect of hyperoxia (normobaric 40% O_2) on male *Drosophila* at 30°C, although females increased by 10% in body mass relative to controls. Overall, the present results and those of Frazier et al. (2001) suggest both phenotypically plastic and heritable responses to oxygen availability, but also inhibitory effects of oxygen when the organisms are suddenly exposed to partial pressures substantially higher than contemporary values. Therefore, future studies of evolutionary responses to hyperoxia should employ smaller increases in oxygen partial pressures over longer time intervals, with multiple generations at each O_2 level, to permit selection on acclimatory responses to increased oxygen availability, e.g., the expression of catalases and superoxide dismutases that mitigate oxidative damage (Orr & Sohal 1994).

As these experiments involve exposure of all life stages to hyperbaria (as well as exposure of the microbial community in the larval growth medium), multiple physiological effects can be expected. Salient among these might be more rapid larval growth (Frazier et al. 2001), enhanced transcuticular diffusion of oxygen into pupae as well as into larvae living within and on the growth medium, and reduced energetic costs of flight in adults deriving from the increased air density (Dudley 2000). Such effects are necessarily conflated in the aforementioned total pressure manipulation, but the overall multigenerational response (Table 2) suggests that historically variable oxygen levels may have played a major role in insect evolution.

The Devonian and Carboniferous were characterized by extensive diversification among the vertebrate tetrapods; the majority of basal tetrapod lineages subsequently went extinct by the end of the Permian (Carroll 1988, Erwin 1993, Graham et al. 1997). Potential physiological consequences of a hyperoxic atmosphere during this important period of terrestrial vertebrate evolution include enhanced cutaneous diffusion and a reduction in the ratio of evaporative water loss to oxygen uptake during pulmonary respiration (Gans 1970, Graham et al. 1997). Increased metabolic capacity, including greater endurance and shortened recovery times from anaerobic bouts, may also have ensued. Somewhat surprisingly, effects of hyperoxia on locomotor performance have never been investigated in extant amphibians and reptiles. Gigantism in some late Paleozoic amphibians (Carroll 1988) may also have derived from enhanced cutaneous diffusion given the importance of this mechanism for large extant amphibians (Ultsch 1974). Unfortunately, present fossil evidence is inadequate to infer the relative importance of different respiratory modes in these now extinct taxa.

O_2 AND PALEOFIRES

Theoretical models of atmospheric oxygen (Berner & Canfield 1989, Berner 2001) suggest that the oxygen content of the atmosphere varied considerably over Phanerozoic time. Because fire is sensitive to the atmospheric oxygen mixing ratio, if the model results are correct, oxygen variations should have been reflected by changes in the patterns of ancient fire.

The best-known writings on oxygen variation and fire come from proponents of the Gaia hypothesis, who use fire as evidence that oxygen has not varied beyond the 15% to 25% range (Watson et al. 1978, Lovelock 1988, Kump 1989b, Lenton & Watson 2000). The 15% lower limit on oxygen variation is supported by the continuous presence of charcoal (i.e., fusain) in the fossil record from the Devonian onward (Cope & Chaloner 1980, Chaloner 1989) and experimental evidence that neither wood (Rashbash & Langford 1968) nor paper (Watson 1978) sustains combustion at oxygen concentrations below approximately 15%.

The upper limit is justified by model-based extrapolation of experiments (Watson 1978) that measured time to ignition and rate of fire spread in paper using fuel moisture and ambient oxygen as control variables. This widely-cited upper limit is suspect (Robinson 1989), however, because ignition outcomes were based on (*a*) the use of thermally thin paper as compared to naturally thick plant material, thus artificially maximizing the exposure of the chosen fuel to oxygen; (*b*) lack of consideration of charring as a protective mechanism against further burning [paper is very low in lignin and does not char as readily as natural lignin-rich plant materials (Table 3)]; (*c*) linear extrapolation of ignition data that do not appear to be linear (Watson 1978, pp. 160–62); (*d*) use of moisture contents far less than found in vegetation; (*e*) translation of results from oxygen variation into fuel moisture equivalents; and (*f*) translating fuel moisture equivalents into an index of probability of ignition using a table that has since been replaced by the U.S. Forest Service because it proved unreliable (Deeming et al. 1977).

Watson (1978, p. 263) initially concluded that "the strong possibility exists that at atmospheric O_2 concentrations three or four percent above the present level, fire would have far-reaching effects on tropical rainforest, and indeed on forest vegetation in general." This was later interpreted (Watson et al. 1978, Lenton & Watson 2000) to imply that oxygen concentrations above 25% are incompatible with the existence of forests and, coupled with the continuity of the fossil record of forests, came to be used as evidence that Phanerozoic oxygen concentration never exceeded 25%.

More recent experiments involving solid fuel combustion under variable oxygen atmospheres (see, e.g., Tewarson 1995, Babrauskas 2003) agree with Watson (1978) in showing that increasing oxygen concentration generally increases the peak heat flux and rate of flame spread and decreases the time required for ignition. However, they also show that response patterns vary greatly between materials.

TABLE 3 Propensities to char of different fine fuels. (Robinson, unpublished data; calculated from Sussot 1980)

Material	Comment	Char fraction† (%)
Cellulose filter paper		4.2
Poplar excelsior	Shaved low lignin wood	14.1
Chamise foliage, live	Fire adapted shrub	39.4
Bracken fern fronds, cured	Fire adapted fern	42.0
Ponderosa pine bark	Fire adapted conifer tree	44.3

†Corrected to an ash-free basis, heating at 200°C/min to 500°C.

One feature common to many materials, not observed by Watson (1978), is a region of high sensitivity, where oxygen concentration strongly limits combustion, and a region of low sensitivity, where additional oxygen has little or no effect on combustion behavior. In most cases, sensitivity appears to be lower above 25% oxygen concentration than below it; in many cases, sensitivity tapers off well before 25% oxygen.

Regardless of his experimental results, Watson's prediction (1978) of "far-reaching effects" of fire on forest vegetation under high oxygen atmospheres makes sense when applied to the Late Paleozoic. Reconstructions (Berner & Canfield 1989, Berner 2001) put the Paleozoic rate of oxygen increase at around 0.2 ‰ per Ma—slow enough to support the evolution of extensive and well-developed fire defenses in plants. Jeffry (cited in Komrek 1973, p. 226) notes that in many plants found in Carboniferous coals, including lycopsids and *Calamites*, "the corky layers were well developed on the outside of the plant as a protective device." Komrek (1973) noted the widespread association of probable Carboniferous relic species with fire communities around the globe. More specifically, he observed that after 27 years of annual burning in Georgia pinewoods, four probable Carboniferous relic fern species increased tremendously in the forest understory. These same species disappeared after five years without fire. Likewise, the spatial organization, energy partitioning, reproductive strategies, and bark structure of Carboniferous ecosystems appear to be consistent with those of forests subject to severe fire regimes (Robinson 1989).

Coals from ages that are reconstructed as having high oxygen concentration are notably richer in fusain (Robinson 1991) than coals of other ages. The abundance of fusain in Late Paleozoic sediments—especially Permian coals, which commonly exceed 30% fusain by volume (see, e.g., Glasspool 2000, Robinson 1989)—is hard to explain based on analogy to modern peat-forming environments. The promotion of char-forming chemical reactions is an effective way to create fire-retardants (Nelson 2001); hence, it may be speculated that fusain-richness of the Late Paleozoic is a reflection of floras with well-developed chemical defenses against fire.

Attempts have been made to reconstruct Paleozoic (Falcon-Lang 2000, Scott 2000) fire regimes based on detailed studies of fusain occurence in fusain-rich geological formations. These have yielded information about burning in a few environments, but do not readily lead to inferences about oxygen level—indeed, they do not answer the question of whether the sedimentary evidence represents typical ecological events or localized catastrophic fires, occurring in forests previously dehydrated by climatic or hydrologic change. It is difficult even to reconstruct Recent fire regimes from the nature of charcoal in Recent sediments (Clark et al. 1997); drawing global conclusions about the flammability of ancient floras based on a small number of studies in fusain-rich strata is difficult.

Understanding of the links between wildfire and oxygen is, at this point, dominated by questions and short on answers. Further research could be very fruitful; for example, repetition of Watson's experiments with more realistic fuel models and instrumentation that provides a more comprehensive and realistic parameterization of fire should resolve questions arising from the design behind the few experimental results that are available. Also, systematic extension of Komrek's (1973) observation on the fire ecology of living fossils is needed, with emphasis on identifying the functional characteristics that allow plants to survive fire, and whether those would be effective under high oxygen. Jones & Chaloner (1991) have shown that the cell wall morphology of fusainized woods reflect the temperature of the formative fire event. If an analogous chemical or morphological marker could be found for the abundance of oxygen in the flame environment, it would open the route to a much-clarified understanding of Phanerozoic oxygen history.

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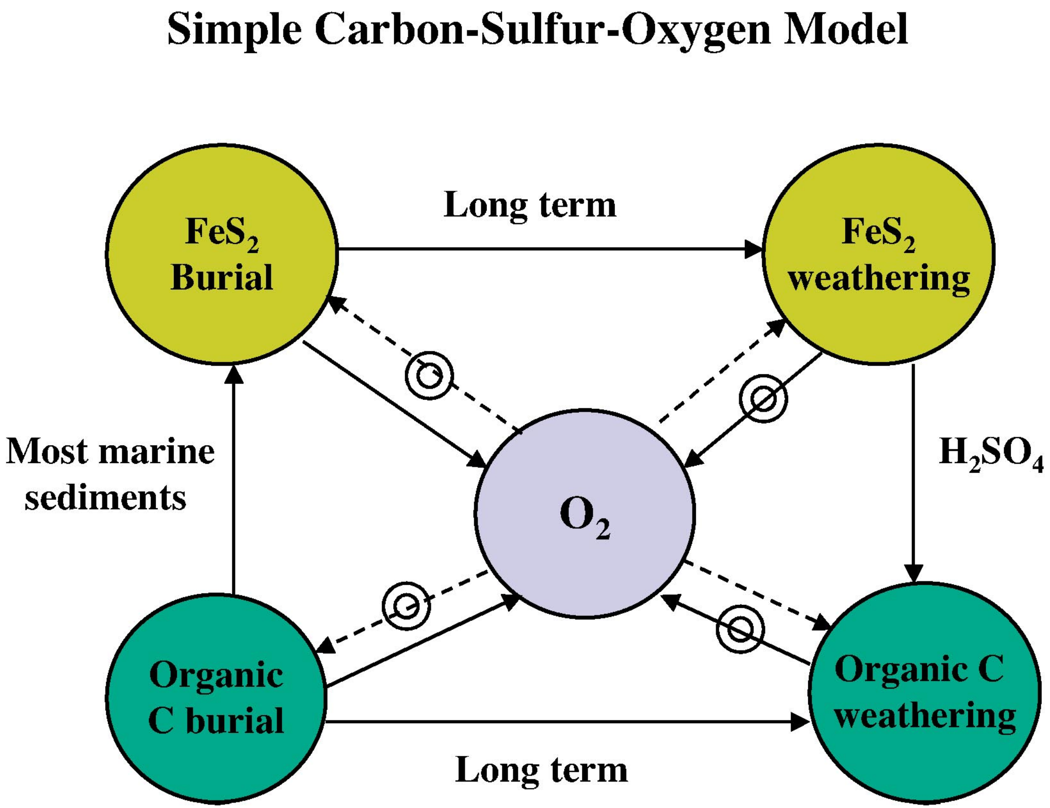

Figure 4 Systems analysis diagram for the simple C–S–O_2 cycle. Dashed arrows represent disputed processes.

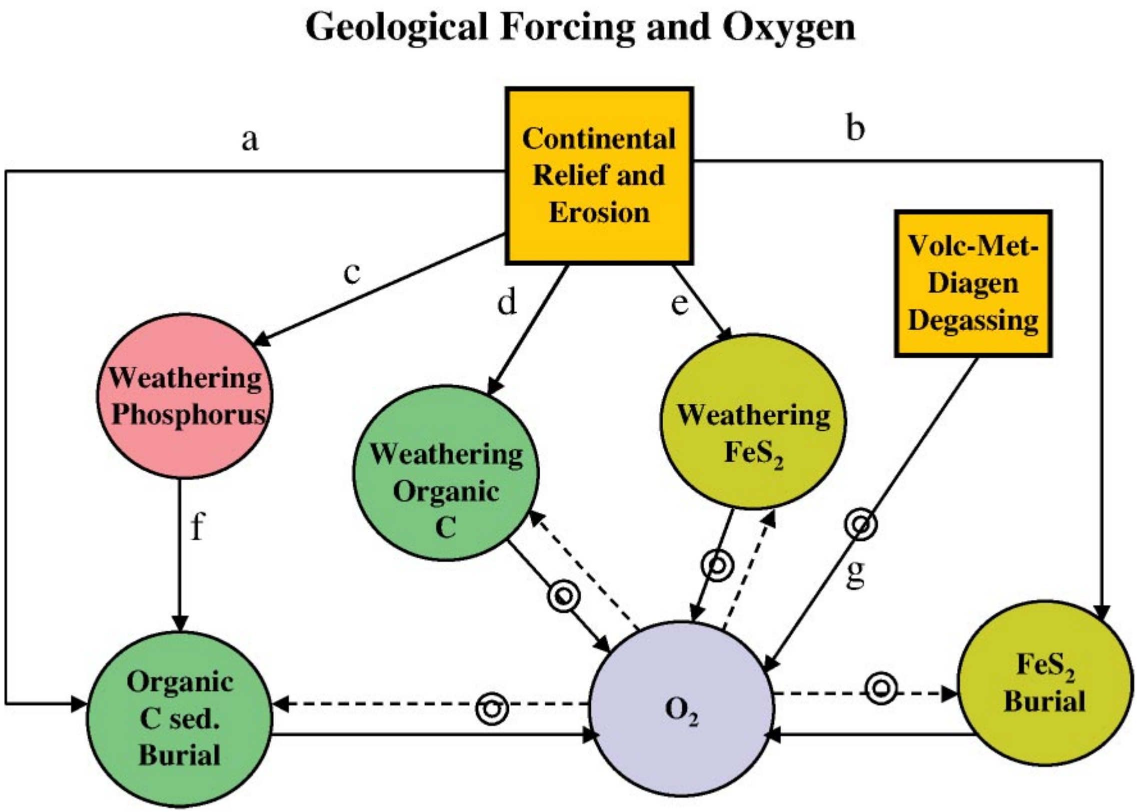

Figure 5 Systems analysis-type diagram emphasizing geological forcing.

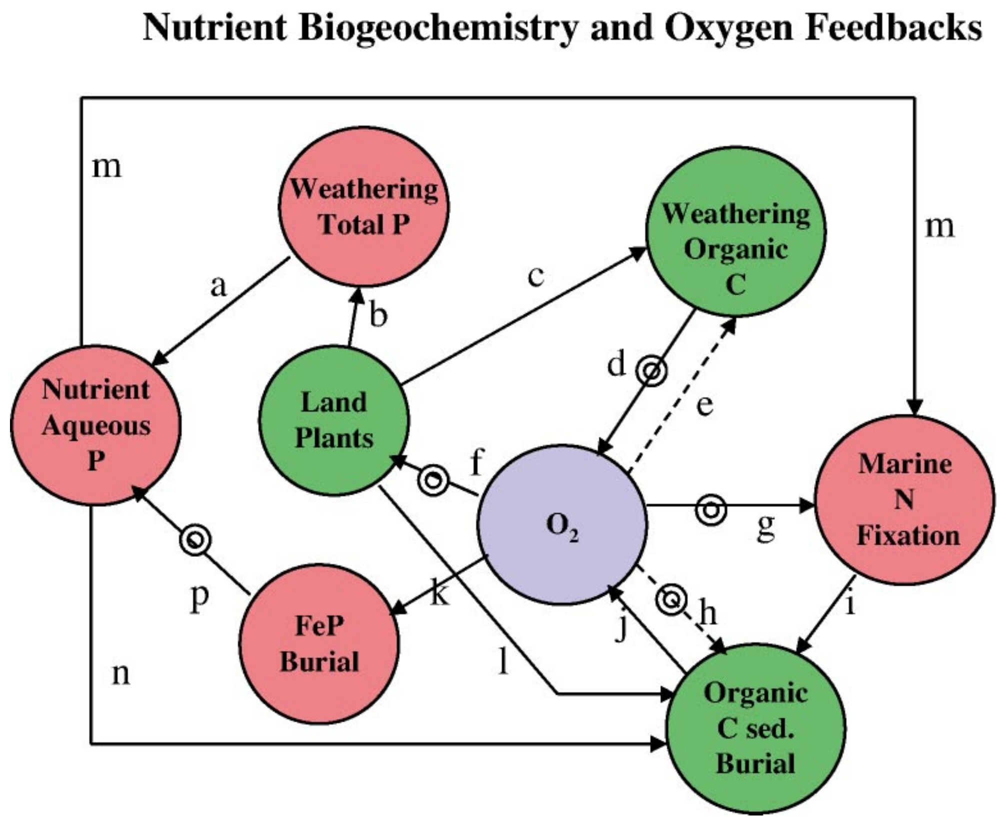

Figure 6 Systems analysis diagram representing nutrient cycling and biogeochemical feedbacks.

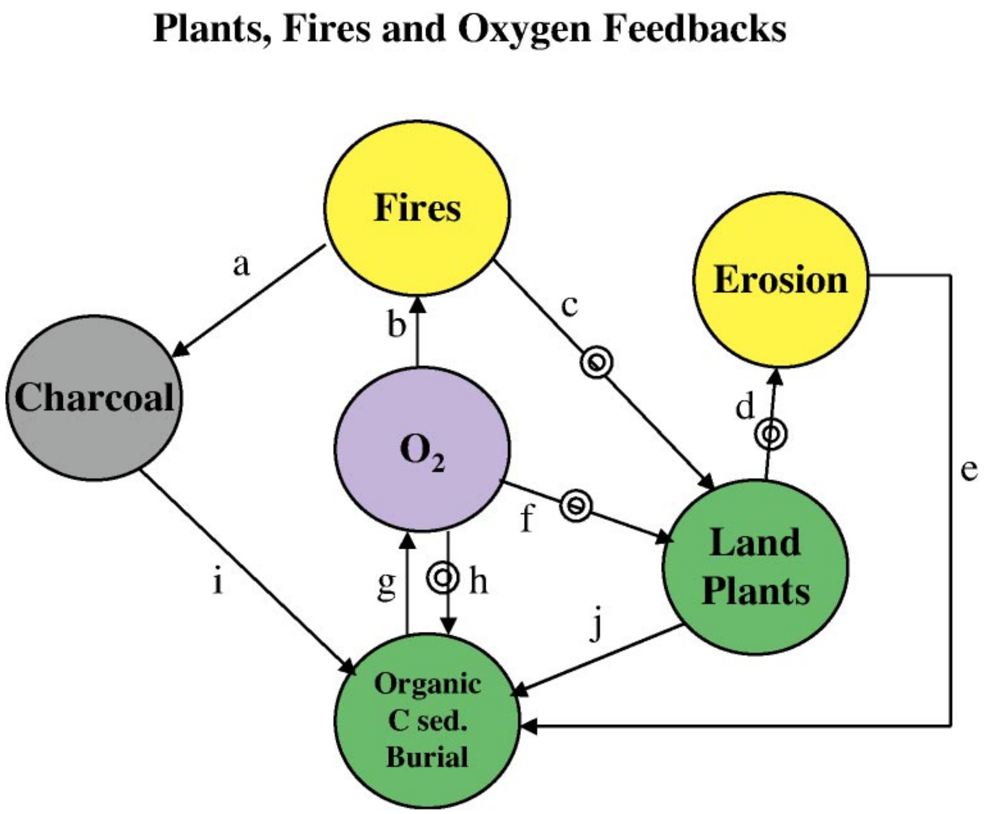

Figure 7 Systems analysis diagram representing the effects of fires on O_2 cycling.

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