PII S0016-7037(00)00572-X

Modeling atmospheric O₂ over Phanerozoic time

R. A. BERNER*

Department of Geology and Geophysics, Yale University, New Haven, CT 06520-8109, USA

Abstract—A carbon and sulfur isotope mass balance model has been constructed for calculating the variation of atmospheric O_2 over Phanerozoic time. In order to obtain realistic O_2 levels, rapid sediment recycling and O_2-dependent isotope fractionation have been employed by the modelling. The dependence of isotope fractionation on O_2 is based, for carbon, on the results of laboratory photosynthesis experiments and, for sulfur, on the observed relation between oxidation/reduction recycling and S-isotope fractionation during early diagenetic pyrite formation. The range of fractionations used in the modeling agree with measurements of Phanerozoic sediments by others.

Results, derived from extensive sensitivity analysis, suggest that there was a positive excursion of O_2 to levels as high as 35% during the Permo-Carboniferous. High O_2 at this time agrees with independent modeling, based on the abundances of organic matter and pyrite in sediments, and with the occurrence of giant insects during this period. The cause of the excursion is believed to be the rise of vascular land plants and the consequent increased production of O_2 by the burial in sediments of lignin-rich organic matter that was resistant to biological decomposition. *Copyright © 2001 Elsevier Science Ltd*

1. INTRODUCTION

The evolution of atmospheric oxygen over geologic time has been a subject of major interest to both the earth and biologic sciences. This is because O_2 is both a principal cause and principal effect of biologic evolution. On shorter time scales atmospheric oxygen concentration represents the balance between production by photosynthesis and consumption by respiration. On a long geologic time scale the level of O_2 is affected by both geological and biologic processes. It is produced by net photosynthesis (photosynthesis minus respiration), represented by the burial of organic matter and pyrite (FeS_2) in sediments, and it is consumed by the oxidation of old buried sedimentary organic matter and pyrite upon uplift and exposure to weathering on the continents. The oxidation of reduced gases produced by the thermal decomposition of organic matter and pyrite at great depths also exerts a control on O_2. (The formation and reduction of iron oxides have only a minor effect on O_2—Holland, 1978).

Although much attention has been given to the rise of O_2 and life during the Precambrian (e.g., Berkner and Marshall, 1965; Cloud, 1976; Walker, 1977; Schidlowski, 1984; Holland, 1984; Des Marais et al.,1992; Canfield and Teske, 1996), little attention has been paid to its continued evolution during the Phanerozoic. Some previous studies (Berner and Canfield, 1989) have suggested that atmospheric oxygen concentrations may have changed appreciably over the Phanerozoic whereas others (e.g., Watson et al., 1978; Lenton and Watson, 2000) have suggested that O_2 has been held essentially constant by strong negative feedbacks.

Recently there has been a lot of interest in negative feedback mechanisms and how they might have controlled Phanerozoic O_2 levels (Holland, 1994; Van Cappellen and Ingall, 1997; Falkowski, 1997; Colman et al., 1998; Lenton and Watson,

2000). Most of this work has focused on the control of organic production in the oceans by nutrient elements such as phosphorus or nitrogen. However, in these studies calculations of O_2 levels as a function of time were not constrained by estimination of actual fluxes of both carbon and sulfur as they affect the input and output of O_2 to and from the atmosphere.

The calculation of past atmospheric oxygen concentrations is possible using the approach pioneered by Garrels and Lerman (1984). This method uses the isotopic record of carbon and sulfur in sedimentary rocks to calculate the rates of the processes that affect O_2 on long time scales, mainly burial in marine sediments and weathering on land of organic matter and biogenic pyrite. Using the Garrels and Lerman model, estimates of the rates of weathering and burial, and their effect on O_2, have been made by Berner (1987), Francois and Gerard (1986), Kump and Garrels (1986), Kump (1989), Lasaga (1989) and Petsch and Berner (1998). However, none of these studies has presented a realistic history of O_2 variations over Phanerozoic time. This is because a key difficulty in this type of modelling is formulating negative feedback mechanisms consistent with both geologic and biologic processes and the isotopic record of carbon and sulfur. Without feedback the modelling leads to calculated variations in O_2 over Phanerozoic time that are biologically and physically impossible, such as large negative values for O_2 concentration during the early Paleozoic.

Initial attempts to include negative feedback in carbon-sulfur models have let the rate of organic matter and pyrite weathering be a direct function of the concentration of atmospheric O_2. In other words as O_2 rises, the rate of its consumption by weathering also rises. However, this approach, although it brings about somewhat damped variations in O_2, still results in impossible O_2 histories (Lasaga, 1989; Berner and Petsch, 1998). With O_2-dependent weathering, positive feedback is unavoidably introduced because of the need for carbon and sulfur isotope mass balance. (For example, if organic C burial suddenly increased, atmospheric O_2 would increase and organic C

*Author to whom correspondence should be addressed (robert.berner@yale.edu).

weathering would also increase if O_2-dependent weathering were present. Although this would help to lower atmospheric O_2, it would also lead to an increased input to the ocean of light carbon from the extra organic weathering necessitating, for steady state, futher increased organic C burial and O_2 production—in other words, positive feedback). In addition, doubt has been placed on whether the rate of O_2 uptake by weathering is actually related to atmospheric O_2 level (Holland, 1978; Holland, 1984; Chang and Berner, 1999). Unavoidable positive feedback is also introduced if the rate of burial of organic matter and/or pyrite are assumed to be an inverse function of atmospheric O_2.

One way to add unencumbered negative feedback to Garrels and Lerman type isotope modelling is to introduce rapid recycling (Berner, 1987). In rapid recycling (see also, Berner and Canfield, 1989) it is assumed that younger rocks that have been deposited more recently are weathered preferentially. In this way rapid variations in the isotopic composition of sediments as they are buried do not result in equally large complementary variations in oceanic isotopic composition because the just-deposited rocks are soon weathered and the anomalous isotopic composition rapidly returned to the ocean. However, calculations show that this approach alone is insufficient to produce realistic O_2 levels and something more is needed.

A mathematical adjustment to Garrels and Lerman-type modelling, that mimics negative feedback while conserving carbon and sulfur mass balance, is to let the fractionation of isotopes during organic matter and pyrite formation be a function of the level of atmospheric O_2. This idea is reasonable. Plant biomass is enriched in ^{12}C relative to CO_2 due to significant isotope discrimination during photosynthesis (e.g., Farquhar et al., 1982). If rates of plant respiration (photorespiration) increase in response to elevated O_2/CO_2, then less rubisco is available for CO_2 fixation and as a result CO_2 builds up in the cell and carbon isotope discrimination is increased. Also, with continued photosynthesis, recycling of the extra photorespiration-derived CO_2 may result in plant biomass that is more enriched in ^{12}C than would be predicted based only on the isotopic composition of ambient, extracellular CO_2. Using this reasoning, we have studied the effect of changing O_2 on carbon isotope discrimination and found enhanced fractionation for both vascular land plants and a marine diatom at elevated O_2 levels (Berner et al., 2000). This has allowed us to introduce a dependence on atmospheric O_2 level to Garrels and Lerman type modelling.

Since the response of fractionation to photosynthesis and photorespiration is a function of both O_2 and CO_2, fractionation can also change with changing CO_2 levels (Hayes et al., 1999). However, the purpose of this paper is to focus on O_2, and as will be seen below, the largest change in fractionation over the Phanerozoic, that occurring during the Permo-Carboniferous, is best explained in terms of changes in O_2, not CO_2. (This conclusion has been verified by unpublished preliminary calculations that let carbon isotope fractionation be a function of O_2 and CO_2 using new laboratory measurements on plants, the determination of $\delta^{13}C$ of plant fossils, and the Phanerozoic CO_2 data of Berner, 1997).

One can also add O_2-dependence to the fractionation of sulfur isotopes during bacterial sulfate reduction and pyrite formation (Berner et al., 2000). This is based on the observation

(Canfield and Teske, 1996) that, in the presence of O_2, sedimentary sulfur undergoes increased isotope fractionation because of multiple cycles of sulfate reduction and sulfide oxidation accompanying the overturn of sediments near the sediment/seawater interface due to bioturbation and wave and current stirring. As atmospheric O_2 increases, it is assumed that, on a global average basis, the extent of oxidation/reduction cycling increases which results in an increase in overall isotope fractionation between seawater sulfate and the pyritic sulfur ultimately buried in sediments.

From the studies of processes controlling O_2, it is reasonable to assume that calculated past O_2 levels should lie within certain extremes. In the present paper limits are defined by the response of forest fires to changing O_2. At sufficiently low O_2 concentration forest fires will not take place, but there is evidence of fires, in the form of fossil charcoal (Chaloner, 1989), for all periods since the rise of woody plants about 425 million years ago. On the other hand, O_2 levels could not have been so high that the destruction of all terrestrial life by fires took place (Watson et al., 1978; Kump, 1989; Robinson, 1989). From these studies and our earlier modeling study (Berner and Canfield, 1989) we have adopted the range 10 to 40% O_2 as a reasonable outside limit for the testing of our model calculations.

In the present paper calculations of the concentration of O_2 over Phanerozoic time are done using the Garrels and Lerman model, modifed to accommodate rapid recycling and O_2-dependent C and S isotope fractionation. By sensitivity analysis, the relative importance of each modification is illustrated. From this analysis, curves of O_2 vs. time can be obtained that are in agreement with laboratory measurements of isotope fractionation and that agree with independent calculations based on the abundance of organic carbon and pyrite sulfur in sedimentary rocks (Berner and Canfield, 1989).

2. METHOD OF CALCULATION

The method of Garrels and Lerman (1984) as adapted by Berner (1987) was used to calculate the rates of weathering and sediment burial of organic carbon and pyrite sulfur (see also Berner and Petsch, 1998). From these data the value of the mass of atmospheric oxygen (O_2) as a function of time can be calculated from the expression:

$$d\,(O_2)/dt = Fbg - Fwg + (15/8)\,(Fbp - Fwp) \qquad (1)$$

where:

Fbg = burial rate of organic C in sediments
Fwg = rate of weathering of organic C (plus minor oxidation of reduced C-containing gases released by volcanism, metamorphism, and deep diagenesis)
Fbp = burial rate of pyrite-s in sediments
Fwp = rate of weathering of pyrite S (plus minor oxidation of reduced S-containing gases released by volcanism, metamorphism, and deep diagenesis)

The concentration of O_2 is calculated from its mass in the atmosphere by assuming a constant mass of N_2 over the Phanerozoic. From the very long residence time of N_2 in the atmosphere (about 300 million years) relative to uptake and release to/from rocks (Holland, 1978) this assumption is reasonable.

The Garrels and Lerman method uses mass balance expresssions for total carbon and sulfur input to the oceans, and output to sediments, and the $^{13}C/^{12}C$ and $^{34}S/^{32}S$ composition of these inputs and outputs. Calculations are based on the isotopic composition of carbon and sulfur in the oceans as a function of time as recorded by carbonates and
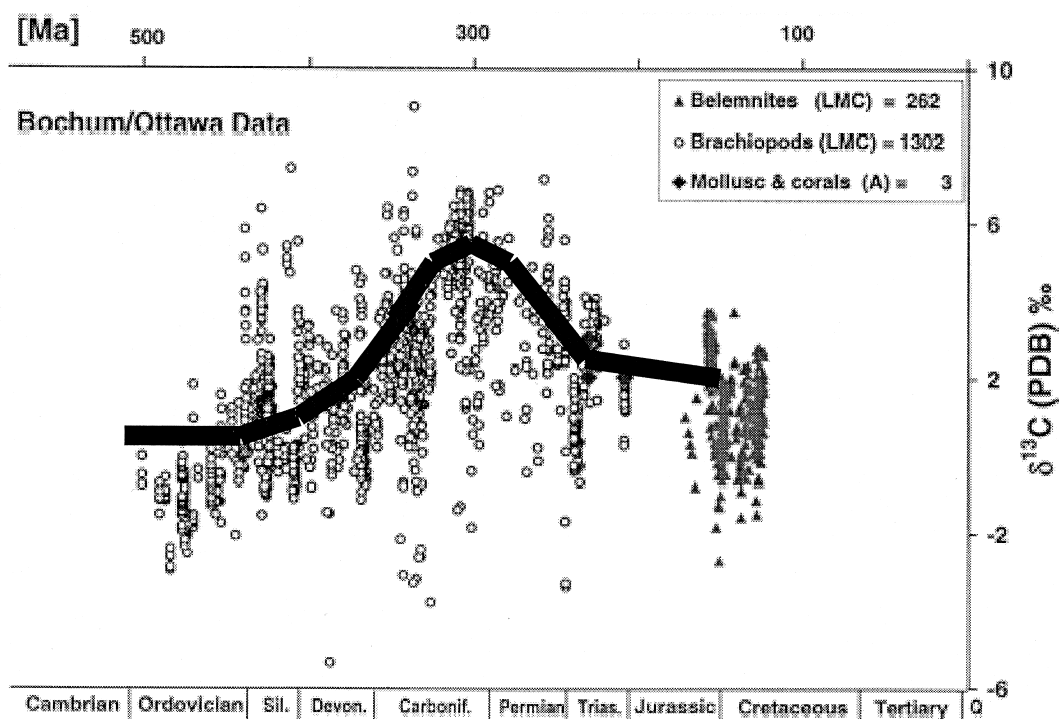
Fig. 1. Simple first order fit to the δ^{13}C measurements of Veizer et al. (1999) on unrecrystallized carbonate fossils. The curve is used in the modeling of the present paper. (Plotted data after Veizer et al., 1999).

sulfates in sedimentary rocks. In the present study isotopic data for the Phanerozoic were taken for carbon from the results of Veizer et al. (1999) for the Ordovician-Cretaceous (Fig. 1) and Lindh (1983) for the remainder of the Phanerozoic. The carbon isotopic data are greatly smoothed to eliminate shorter term variations and, thereby, to show only the first order Phanerozoic trend. (For the Ordovician-Cretaceous only the data actually measured by Veizer et al. are used here, and not those summarized by them from the literature, because of the greater care taken by Veizer et al. in selecting samples for isotopic analysis). Sulfur isotope data are from the compilation by Lindh (1983).

In Garrels and Lerman modeling carbon is added to the ocean/atm system by the weathering of carbonates and organic carbon exposed on land combined with degassing of C-containing gases via the metamorphic, volcanic and diagenetic breakdown of deeply buried organic C and carbonates. Carbon is removed by the burial of organic matter and Ca and Mg carbonates in sediments. Sulfur is added to the ocean/atm system by the weathering of pyrite (FeS$_2$) and CaSO$_4$ minerals (plus degassing from the thermal breakdown of both minerals) and removed by the burial of newly formed mixtures of these minerals in sediments. At each time step the masses of the four reservoirs, organic carbon, carbonate carbon, sulfide sulfur, and sulfate sulfur, and their isotopic compositions are recalculated. From these data, combined weathering plus metamorphic release rates are calculated from the assumption of a direct proportionality of flux to the mass of each reservoir present at each time. The calculations are set up so that present day masses and fluxes are obtained at the end of each computer run.

Negative feedback was added to the Garrels and Lerman model by employing rapid recycling (Berner, 1987; Berner and Canfield, 1989). In this method the mass of each reservoir is divided into young, rapidly weathering and old, slowly weathering subreservoirs. The young subreservoirs were assumed to be 25% the mass of the old reservoirs and to weather ten times faster. This means that the mean residence time of the fast-weathering reservoirs to loss by weathering was assumed to be 35 to 75 million years. This is a reasonable representation of the area-weighted mean age of sedimentary rocks presently exposed to weathering at the earth's surface. All burial of carbon and sulfur necessarily goes to the young reservoirs. This method provides nega-

tive feedback to the system by allowing for the fact that, due to sea level changes, sediments deposited more recently are more likely to be exposed to weathering on the continents since they overlie the older sediments.

An important additional modification to the Garrels and Lerman modelling was done by making the fractionation of carbon istopes between carbonate and organic matter (due to photosynthesis) and sulfur isotopes between sulfate and sulfide (due to bacterial sulfate reduction) be a function of the level of atmospheric O$_2$. (The effect of CO$_2$ on fractionation is discussed below.) Here is employed a function that agrees with the results of plant and plankton growth experiments (Berner et al., 2000) and photosynthetic theory for land plants (Farquhar et al., 1982; Farquhar and Wong, 1984; see also Berner et al., 2000):

$$\Delta_{c\,(phot)} \approx \delta^{13}C_{CO_2} - \delta^{13}C_{organic} = \Delta_{c(phot)}(0)$$
$$+ J((O_2/38) - 1) \quad (2)$$

where:

$\Delta_{c(phot)}$ = isotope fractionation (discrimination) of carbon (in ‰) during photosynthesis $\Delta_{c(phot)}(0) = \Delta_c$ (phot) value for the present level of O$_2$ but for an average higher CO$_2$ level during the Phanerozoic (Berner, 1997; Hayes et al., 1999)

O_2 = mass of oxygen in the atmosphere

38 = mass of oxygen in the present atmosphere (in 10^{18} moles)

J = adjustable curve-fit parameter

Values of J were varied until there was agreement of the expression with the results of the plant and plankton growth experiments. The physical interpretation of J is complex; for present purposes it can be thought of simply as the strength of the effect of O$_2$ on ^{13}C isotope fractionation during photosynthesis for a fixed level of CO$_2$. (Presently undertaken laboratory experiments on plants by D. J. Beerling show that J can be expressed as a function of CO$_2$, without causing major change in the calculated results for O$_2$ over time.)

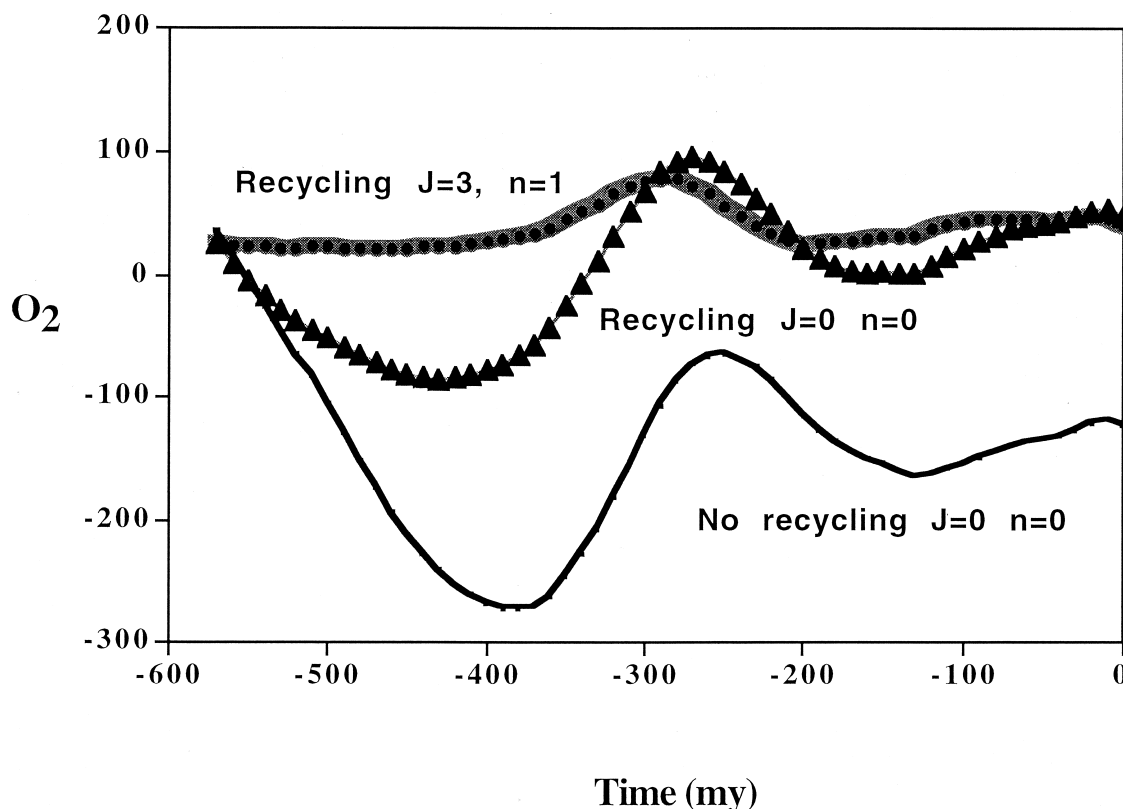Because the modeling uses the difference in δ^{13}C between calcium

Fig. 2. Sensitivity of O_2 vs. time to the addition of rapid recycling and O_2-dependence of carbon isotope fractionation $(J = 3, n = 1)$ to isotope mass balance modeling with $\Delta_c(0) = 25‰$. O_2 is expressed in 10^{18} moles. The situation for no O_2-dependence is signified by $J = 0, n = 0$. For the definitions of J and n see text Eqns. 2 and 3.

carbonate and organic matter buried in sediments (Δ_c), it is necessary to calculate the value of Δ_c from $\Delta_c(phot)$. This involves correcting for the fractionation between CO_2 and $CaCO_3$ which varies with temperature, and for changes in $\delta^{13}C$ of organic matter due to food-chain processing and diagenesis (Hayes et al., 1999). Because this paper focuses only on O_2-dependent photosynthetic fractionation, these other fractionations are assumed to remain constant over time. (A complete model for the change of fractionation with time would allow for temperature change, changes in organic processing, and changes in CO_2 as discussed below.) On this basis, Δ_c can be substituted for $\Delta_c(phot)$ and $\Delta_c(0)$ for $\Delta_c(phot)(0)$ in Eqn. 2 because of the assumption of a constant offset over time between $\Delta_c(phot)$ and Δ_c.

For sulfur a simple positive dependence function was used, based on the observation of greater fractionation with higher atmospheric O_2 (Canfield and Teske, 1996)

$$\Delta_s \approx \delta^{34}S_{sulfate} - \delta^{34}S_{sulfide} = \Delta_{s(0)}(O_2/38)^n \qquad (3)$$

where:

Δ_s = fractionation for sulfur (in ‰)
$\Delta_s(0)$ = fractionation for the present level of O_2 (35‰)
  n = arbitrary parameter

Experiments to derive a better defined dependence would be virtually impossible because of the occurrence under natural conditions of (1) the variability of isotope fractionation during sulfate reduction which depends on such things as rate of reduction, nature of the carbon source and temperature (Canfield et al., 2000); (2) the extent of sulfate reduction (closed vs open system in sediments); (3) the time of pyrite formation (syngenetic vs diagenetic); and (4) additional fractionation accompanying sedimentary reoxidation/disproportionation during the recycling of sulfur in sediments by bioturbation and wave and current stirring. If reoxidation/disproportionation from bioturbation and wave

and current stirring is enhanced by greater levels of atmospheric O_2 (Canfield and Teske, 1996), then a reasonable first approximation is to let fractionation be a direct function of O_2 concentration. This is what is done here.

As a check on our modeling of carbon and sulfur isotope fractionations we have used compilations for the measured difference in isotopic composition between organic carbon and carbonate carbon (Hayes et al., 1999) and pyrite sulfur and $CaSO_4$-sulfur (Strauss, 1999) for Phanerozoic sediments. This "ground truth" provides an additional test to the results of our modeling.

3. RESULTS

Figures 2–9 show the sensitivity of varying different input parameters to the values of O_2 mass as a function of time. In Figures 2 to 4 oxygen is expressed as total mass in the atmosphere in 10^{18} moles. Figure 2 shows the effects of adding rapid recycling and oxygen dependency to both carbon and sulfur isotope fractionation. The symbols J and n represent the curve fit parameters of Eqn. 2 and (3). Figures 3 is an expansion of Figure 2 for later times and also includes the effects of O_2-dependent C and S isotope fractionation alone. Figures 4 and 5 illustrate the variation of carbon isotope fractionation over time based on varying values of J in Eqn. 2 and with comparsion to the C isotope data of Hayes et al. (1999). Figures 6 and 7 show how sulfur isotope fractionation varies with varying values of n in Eqn. 3 with comparison of results to the results of Strauss (1999). In Figure 8 sensitivity to change in the effect of the value chosen for the fractionation of carbon isotopes at present
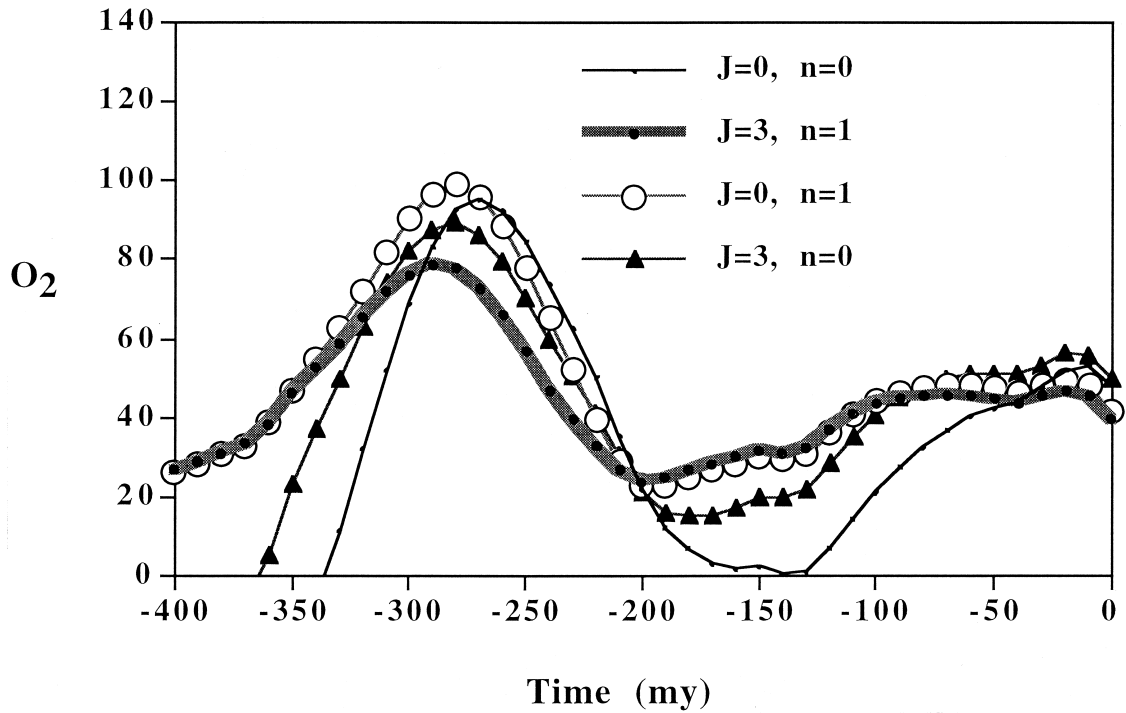
Fig. 3. Sensitivity of O$_2$ vs. time plots to the addition of O$_2$-dependence of carbon isotope fractionation (J = 3, n = 0), sulfur isotope fractionation (J = 0, n = 1) and both (J = 3, n = 1) for the period of 400 my to the present. ($\Delta_c(0)$ = 25‰, rapid recycling).
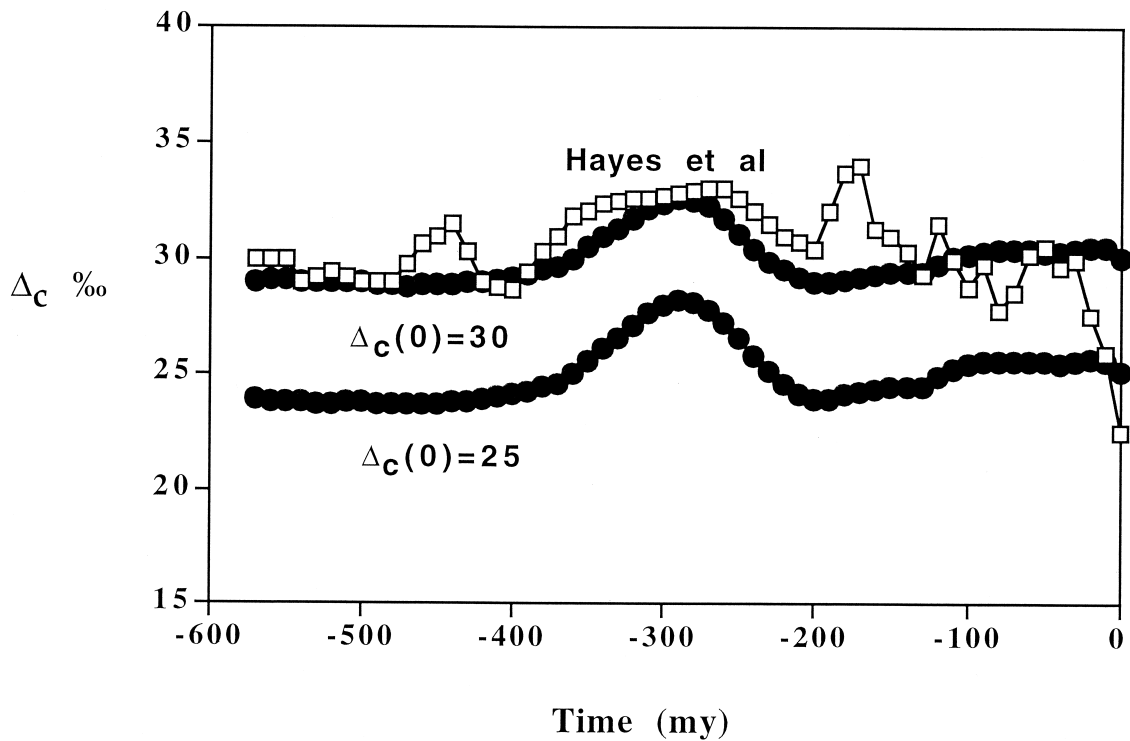

Fig. 4. Plots of carbon isotope fractionation Δ_c vs. time for J = 3, n = 1 and $\Delta_c(0)$ = 25‰, 30‰ compared with the measured values for sedimentary carbonates and bulk organic matter compiled by Hayes et al. (1999).
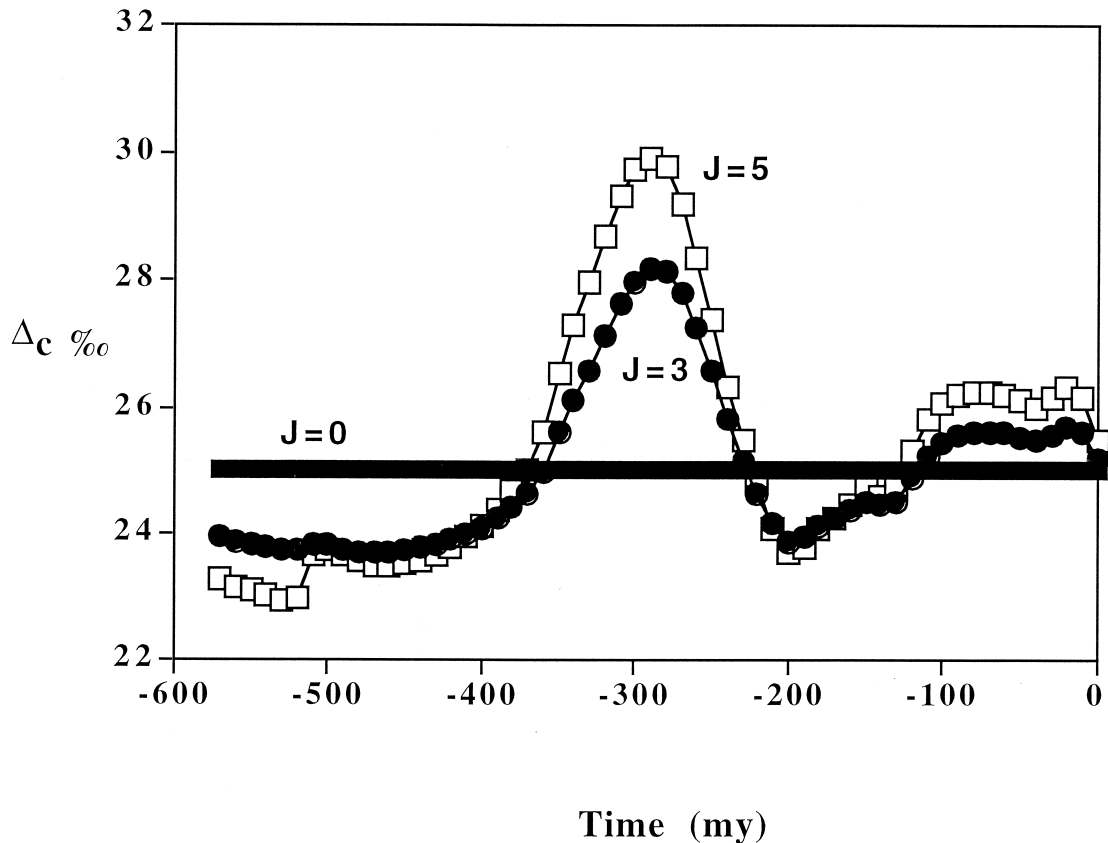
Fig. 5. Plots of carbon isotope fractionation Δ_c vs. time for different values of J and n = 1. ($\Delta_c(0)$ = 25‰, rapid recycling).

4. DISCUSSION

$\Delta_c(0)$ is demonstrated. Finally best estimates of atmospheric O_2 over Phanerozoic time, in terms of % O_2, are shown in Figure 9 and compared to the results of Berner and Canfield (1989) based on sediment abundance data for organic carbon and pyrite sulfur.

4. DISCUSSION

Using constant values over time for the fractionation of carbon and sulfur isotopes, the effect of including rapid recycling in carbon and sulfur isotope mass balance modeling results in an improved curve of O_2 vs. time, but the results still shows impossibly large excursions (Fig. 2). The excursions are greatly reduced by adding the dependence of carbon and sulfur isotope fractionation on O_2 (J = 3 and n = 1—see Eqn. 2 and 3). From Figure 3 it is apparent that the improvement in the O_2-vs time curve is due to the inclusion in the modelling of oxygen-dependent isotope fractionation for both carbon and sulfur but with a greater effect for sulfur for the early Paleozoic.

Carbon isotope fractionation vs time, expressed as carbonate-C minus organic-C, calculated using J = 3 in Eqn. 2 and n = 1 in Eqn. 3 is shown in Figure 4 and compared with the data of Hayes et al. (1999). For sensitivity analysis two values of $\Delta_c(0)$ were used: 25‰ and 30‰. So as to retain the simple O_2-dependence of our model, no attempt was made to match the actual changes of Δ_c reported by Hayes et al., especially those over the Cenozoic. The generally higher past values

shown by the Hayes et al. data is attributed mainly to the effect of higher CO_2 levels over most of the geologic past in producing enhanced carbon isotope fractionation during photosynthesis (Freeman and Hayes, 1992). All three curves show a positive excursion during the middle Paleozoic centered around 300 Ma which we believe was due to higher levels of O_2 at that time.

It is less likely that the 300 ma excursion is due to a rise in CO_2 which could also bring about greater fractionation. This is partly because terrestrially-derived plant debris was the major source for buried organic matter during this time (Berner and Raiswell, 1983) and land plants exhibit much lower sensitivity of carbon isotope fractionation to changes in atmospheric CO_2 (Polley et al., 1993; Beerling. 1996; Arens et al., 2000). Also, independent studies (for a summary consult Berner, 1997) indicate that there was most likely *lower* CO_2 during this period compared to CO_2 levels previously and subsequently. Further, unpublished experiments of carbon isotope fractionation, as a function of O_2/CO_2, by a variety of land plants combined with determination of the $\delta^{13}C$ of fossil plants (Beerling, ms in preparation) show that variations in O_2, and not CO_2 best explain the inctrease in fractionation during the Permo-Carboniferous. It is important to note that the use of either the Hayes et al. curve or either of ours from Figure 4 results in similar plots of O_2 vs. time (see below).

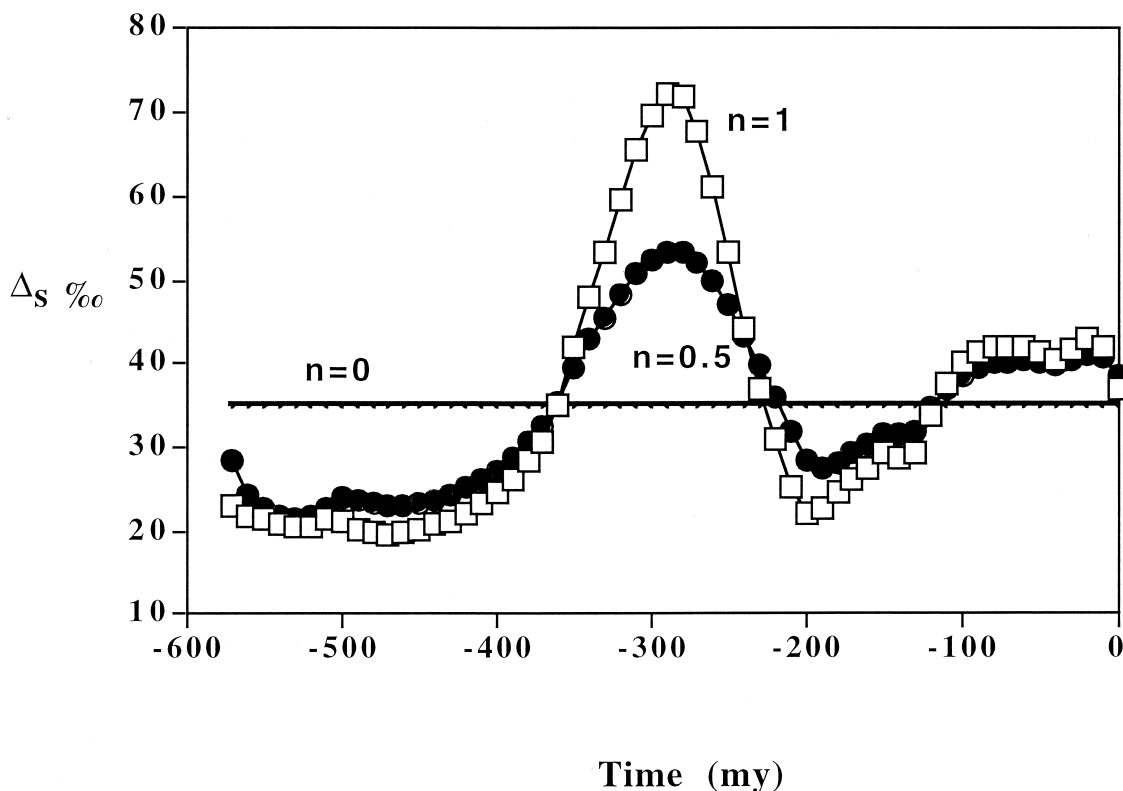Figure 5 demonstrates how the variation of Δ_c with O_2 over

Fig. 6. Plots of sulfur isotope fractionation Δ_s vs. time for different values of n and J = 3. ($\Delta_c(0)$ = 25‰, rapid recycling).

time depends on the value of J in Eqn. 2. Laboratory measurements of carbon isotope discrimination by vascular land plants (one flowering plant and one cycad) and marine plankton (a species of diatom) are fit best by J = 2 to 3 (Berner et al., 2000). Because of this, the curve labelled J = 3 in Figure 5 is preferred.

Sensitivity of sulfur isotope fractionation to variations in the exponent n is shown in Figure 6. The variation of the measured degree of sulfur isotope fractionation between sedimentary pyrite and seawater sulfate (as recorded by sulfate in evaporites and incorporated into calcium carbonate) has been summarized by Strauss (1999) for Phanerozoic sediments. In Figure 7 Strauss' results are compared to the calculated value for J = 3, n = 0.5. Considering the many factors that affect sulfur isotope fractionation during sedimentary pyrite formation and how they could have varied over Phanerozoic time (Canfield and Teske, 1996), the calculated and observed data fall well within the same range. (Note the very large range in the results compiled by Strauss for each time period which would likely expand as more pyrite samples in older rocks are analyzed.)

Sensitivity of O_2 vs time to change in the present carbon isotope fractionation between carbonate-C and organic-C ($\Delta_c(0)$ = 25‰ and 30‰) is shown in Figure 8. The similar results demonstrate the relative insensitivity to the value chosen for the Phanerozoic mean value (see Fig. 4) which, in each case is similar to that for the present day. This is agrement with the earlier sensitivity studies of Kump (1989) and Lasaga (1989).

Figure 9 shows three best estimates (J = 3, n = 0.5, $\Delta_c(0)$ = 25‰; J = 3, n = 1, $\Delta_c(0)$ = 30‰; and Hayes Δ_c, n = 1) of the

variation of O_2 over Phanerozoic time based on Garrels and Lerman isotope mass balance modeling with rapid recycling. Also included in Figure 9 is a plot of O_2 vs. time from the results of Berner and Canfield (1989). The Berner and Canfield results are based on a completely independent method where burial fluxes are calculated from the abundance of organic C and pyrite S in sedimentary rocks as a function of time, and no isotopic data are used. One goal of the present study was to see if a plot of O_2 vs time could be derived from isotope mass balance modelling which could be compared with that based on rock abundance. By choosing the appropriate expressions for the O_2 dependence of C and S isotope fractionation and employing rapid recycling, it was possible to obain three curves in good agreement, with the rock abundance-based results (within the errors of the Berner and Canfield estimates). This is shown in Figure 9 and it gives some credence to the idea that both methods of theoretical modeling provide some idea of the variation of atmospheric O_2 over Phanerozoic time.

The most obvious feature of Figure 9 is the large maximum in O_2 centered around 300 million years BP. The explanation for this has been given earlier (Holland, 1978; Berner, 1987; Berner and Canfield, 1989) and involves the rise of large vascular land plants on the continents. The production of abundant new sources of microbially resistant organic matter, especially lignin, should have led to greater burial of organic C, both in terrestrial swamps and in the sea after being carried there by rivers. This greatly enhanced burial led to the formation of vast coal deposits (the largest for all geologic time) and the excessive production of O_2. The evidence for this is the
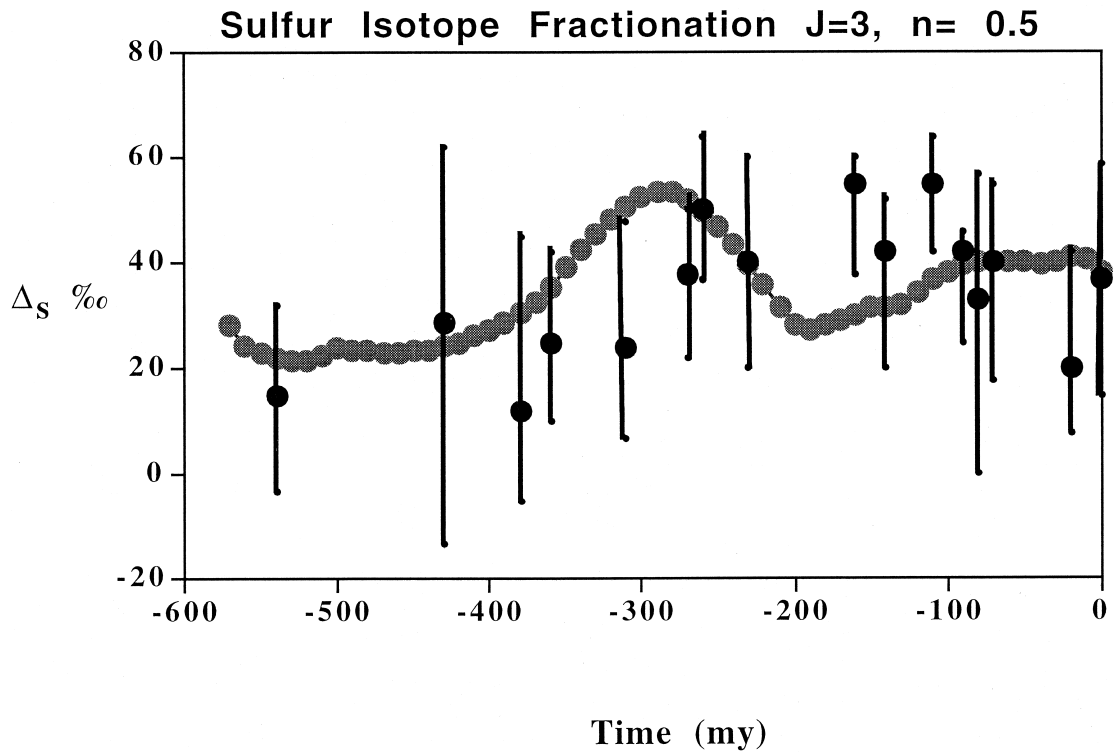
Fig. 7. Plot of sulfur isotope fractionation Δ_s vs. time for J = 3, n = 0.5 compared with the compilation of sulfur isotope measurements by Strauss (1999).
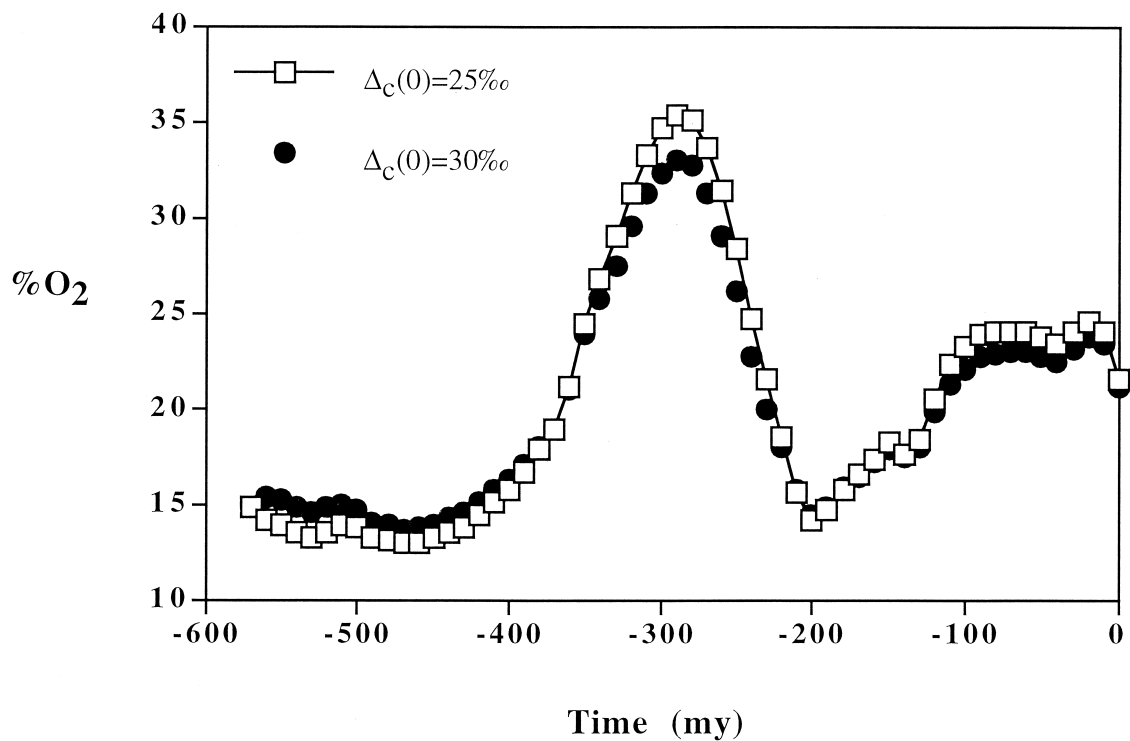

Fig. 8. Plots of O_2 vs. time for $\Delta_c(0)$ = 25‰ and 30‰, J = 3 (Eqn. 2) and n = 1 (Eqn. 3). This shows the relative insensitivity of O_2 to the present value for carbon isotope fractionation (see Fig. 4).
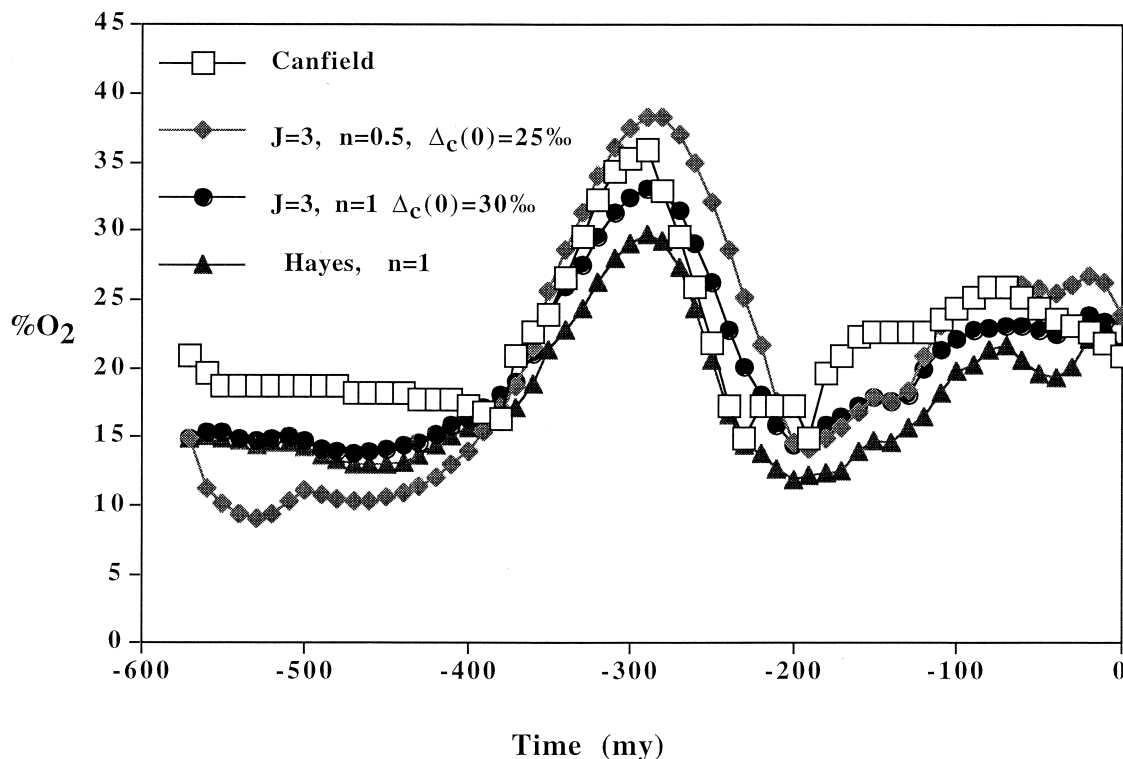
Fig. 9. Plots of % O_2 vs. time for the Phanerozoic calculated in three ways by isotope mass balance modeling (present study) and by the abundance of organic C and pyrite S in sedimentary rocks (Berner and Canfield, 1989 denoted as Canfield). J, n, and $\Delta_c(0)$ refer to Eqn. 2 and 3 of the text; Hayes refers to Δ_c values reported by Hayes et al. (1999). (Constant mass of atmospheric N_2 is assumed in calculating %O_2 from its atmospheric mass.).

large increase in ^{13}C of the ocean (plus atmosphere) at that time (Berner, 1987) due to an increased removal of ^{12}C from seawater and the atmosphere as organic matter buried in sediments. This idea is confirmed by the calculations of Berner and Canfield (1989) who show that, due the abundance of organic carbon-rich coal basin sediments, global organic C burial was considerably elevated during the Permo-Carboniferous. This helps explain the agreement of our O_2 curve with that of Berner and Canfield.

Such high levels of O_2 for the Permo-Carboniferous have encountered objections. Watson et al. (1978) and Lenton and Watson (2000) have stated that levels of O_2 could not have risen at any time higher than about 25% because otherwise vast global forest fires would have wiped out all plant life. Their results are based on the experimental ignition of paper strips at different O_2 levels and degrees of moisture. However, the application of paper strip ignition to the ecology of forest burning has been severely criticized by Robinson (1989) who, on the contrary, has presented evidence for more fire-resistant plants during the Permo-Carboniferous as evidence of higher O_2 levels. We feel that experiments on burning under more natural conditions are needed before one can place firm limits on forest fire frequency as a function of O_2 level.

Some recent physiologic studies have shown that higher O_2 levels during the Permo-Carboniferous could help explain a number of observations of fossil animals. Graham et al. (1995) and Dudley (1998) have suggested that much of the gigantism of insects, changes in marine organisms with diffusion-medi-

ated respiration, and the invasion of land by vertebrates at this time may have been due to elevated O_2. In agreement with this reasoning, Harrison and Leighton (1998) have found from experiments that elevated O_2 enhances flight metabolism in dragonflies and they have used this observation as a possible explanation for the presence of giant dragonflies (up to 70 cm wing span) that flourished during the Carboniferous. In addition to animal physiologic considerations, Beerling et al. (1998) have shown that plants can survive and grow at elevated O_2 concentrations as suggested here for the Permo-Carboniferous.

5. CONCLUSIONS

Isotope mass balance calculations along with the earlier calculations based on the abundances of pyrite and organic matter in sedimentary rocks, have led to the conclusion that the level of atmospheric O_2 has varied considerably over Phanerozoic time, reaching a peak during the Permo-Carboniferous that was brought about by the rise of large vascular land plants. The calculated concentrations fall within reasonable limits, but much more modeling is needed before one can say anything more definite about absolute past concentrations of O_2. Better models are needed that include the effects of varying CO_2 and temperature on isotope fractionation (Hayes et al., 1999) and the effects of factors, such as climate and relief, that affect weathering rates (e.g., Berner, 1994). Also needed to guide the modeling is more experimental plant and plankton growth studies and more experimental animal metabolism studies, both

conducted on organisms representative of those living during the distant geological past. These studies. along with further investigation of the response of forest fires to changing O_2 levels, should go far in helping to further knowledge of the evolution of the atmosphere over geologic time.

Associate editor: K. Freeman

REFERENCES

Arens N. C., Jahren A. H., and Amundson R. (2000) Can C3 plants faithfully record the carbon isotope composition of atmospheric carbon dioxide? *Paleobiology* **26,** 137–164.

Beerling D. J. (1996) ^{13}C discrimination by fossil leaves during the late-glacial climate oscillation 12–10 ka BP: Measurements and physiological controls. *Oecologia.* **108,** 29–37.

Beerling D. J., Woodward F. I., Lomas M. R., Wills M. A., Quick W. P., and Valdes P. J. (1998) The influence of Carboniferous paleoatmospheres on plant function: An experimental and modeling assessment. *Phil. Trans. Roy. Soc. Series B* **353,** 131–140.

Berkner L. V. and Marshall L. C. (1965) On the origin and rise of oxygen concentration in the Earth's atmosphere. *J. Atm. Sci.* **22,** 225–261.

Berner R. A. (1987) Models for carbon and sulfur cycles and atmospheric oxygen: Application to Paleozoic geologic history. *Am. J. Sci.* **287,** 177–190.

Berner R. A. (1997) The rise of plants and their effect on weathering and atmospheric CO_2. *Science* **276,** 544–546.

Berner R. A. and Canfield D. E. (1989) A new model of atmospheric oxygen over Phanerozoic time. *Am. J. Sci.* **289,** 333–361.

Berner R. A. and Petsch S. T. (1998) The sulfur cycle and atmospheric oxygen. *Science* **282,** 1426–1427.

Berner R. A., Petsch S. T., Lake J. A., Beerling D. J., Popp B. N., Lane R. S., Laws E. A., Westley M. B., Cassar N., Woodward F. I., and Quick W. P. (2000). Isotope fractionation and atmospheric oxygen: Implications for Phanerozoic O_2 evolution. *Science* **287,** 1630–1633.

Berner R. A. and Raiswell R. (1983) Burial of organic carbon and pyrite sulfur in sediments over Phanerozoic time: a new theory. *Geochim. Cosmochim. Acta* **47,** 855–862.

Canfield D. E., Habicht K. S., and Thamdrup B. (2000) The. Archean sulfur cycle and the early history of atmospheric oxygen. *Science* **288,** 658–661.

Canfield D. E. and Teske A. (1996) Late Proterozoic rise in atmospheric oxygen concentration inferred from phylogenetic and sulphur-isotope studies. *Science* **382,** 127–132.

Chaloner W. G. (1989) Fossil charcoal as an indicator of paleoatmospheric oxygen level. *J. Geol. Soc. London* **146,** 171–174.

Chang S. and Berner R. A. (1999) Coal weathering and the geochemical carbon cycle. *Geochim. Cosmochim. Acta* **63,** 3301–3310.

Cloud P. E. (1976) Beginnings of biospheric evolution and their biogeochemical consequences. *Paleobiology* **2,** 351–387.

Colman A. S., Mackenzie F. T., and Holland H. D. (1998) Redox stabilization of the atmosphere and oceans and marine productivity. *Science* **275,** 406–407.

Des Marais D. J., Strauss H., Summons R. E., and Hayes J. M. (1992) Carbon isotope evidence for the stepwise oxidation of the Proterozoic environment. *Nature* **359,** 605–609.

Dudley R. (1998) Atmospheric oxygen, giant Paleozoic insects and the evolution of aerial locomotor performance. *J. Exp. Biol.* **201,** 1043–1050.

Falkowski P. G. (1997) Evolution of the nitrogen cycle and its influence on the biological sequestration of CO_2 in the ocean. *Nature* **387,** 272–275.

Farquhar G. D., O'Leary M. H., and Berry J. A. (1982) On the relationship between carbon isotope discrimination and the inter-cellular carbon-dioxide concentration in leaves. *Aust. J. Plant. Physiol.* **9,** 121–137.

Farquhar G. D. and Wong S. C. (1984) An empirical-model of stomatal conductance. *Aust. J. Plant. Physiol.* **11,** 191–209.

Francois L. M. and Gerard J. C. (1986) A numerical model of the evolution of ocean sulfate and sedimentary sulfur during the past 800 million years. *Geochim. Cosmochim. Acta* **50,** 2289–2302.

Freeman K. H. and Hayes J. M. (1992) Fractionation of carbon isotopes by phytoplankton and estimates of ancient CO_2 levels. *Glob. Biogeochem. Cyc.* **6,** 185–198.

Garrels R. M. and Lerman A. (1984) Coupling of the sedimentary sulfur and carbon cycles-an improved model. *Am. J. Sci.* **284,** 989–1007.

Graham J. B., Dudley R., Aguilar N. M., and Gans C. (1995) Implications of the late Paleozoic oxygen pulse for physiology and evolution. *Nature* **375,** 117–120.

Harrison J. F. and Lighton J. R. B. (1998) Oxygen-sensitive flight metabolism in the dragonfly *Erythemus simplicicollis. J. Exp. Biol.* **201,** 1739–1744.

Hayes J. M, Strauss H., and Kaufman A. J. (1999) The abundance of ^{13}C in marine organic matter and isotope fractionation in the global biogeochemical cycle of carbon during the past 800 Ma. *Chem. Geol.* **161,** 103–125.

Holland H. D. (1978) The chemistry of the atmosphere and oceans. New York: Wiley Interscience.

Holland H. D. (1984) The chemical evolution of the atmosphere and oceans. Princeton, Princeton Univ. Press, 582 p.

Holland H. D. (1994) The phosphate-oxygen connection. *EOS, Trans. Am. Geophys. Union.* **75,** No.3., p. OS96

Kump L. R. (1988) Terrestrial feedback in atmospheric oxygen regulation by fire and phosphorus. *Nature* **335,** 152–154.

Kump L. R. (1989) Alternative modeling approaches to the geochemical cycles of carbon, sulfur and strontium isotopes. *Am. J. Sci.* **289,** 390–410.

Kump L. R. and Garrels R. M. (1986) Modeling atmospheric O_2 in the global sedimentary redox cycle. *Am. J. Sci.* **286,** 336–360.

Lasaga A. C. (1989) A new approach to the isotopic modeling of the variation of atmospheric oxygen through the Phanerozoic. *Am. J. Sci.* **298,** 411–435.

Lenton T. M. and Watson A. J. (2000) Redfield revisited 2. What regulates the oxygen content of the atmosphere? *Glob. Biogeochem. Cycles.* **14,** 249–268.

Lindh T. B. (1983) Temporal variations in ^{13}C and ^{34}S and global sedimentation during the Phanerozoic. Thesis. Univ. Miami. 98 pp (unpublished).

Petsch S. T. and Berner R. A. (1998) Coupling the long-term geochemical cycles of carbon, phosphorus, sulfur, and iron: the effect on atmospheric O_2 and the isotopic records of carbon and sulfur. *Am. J. Sci.* **298,** 246–262.

Polley H. W., Johnson H. B., Marino B. D., and Mayeux H. S. (1993) Increase in C3 plant water-use efficiency and biomass over glacial to present CO_2 concentrations. *Nature.* **361,** 61–64.

Robinson J. M. (1989) Phanerozoic O_2 variation, fire, and terrestrial ecology. *Paleogeog. Paleoclim. Paleoecol.* **75,** 223–240.

Schidlowski M. (1984) Early atmospheric oxygen levels: constraints from Archaen photoautotrophy. *J. Geol. Soc. London.* **141,** 243–250.

Strauss H. (1999) Geological evolution from isotope proxy signals—sulfur. *Chem. Geol.* **161,** 89–101.

Van Cappellen P. and Ingall E. D. (1997) Redox stabilization of the atmosphere and oceans by phosphorus-limited marine productivity. *Science* **271,** 493–496.

Veizer J., Ala D. Azmy K., Bruckschen P., Buhl D., Bruhn F., Carden G. A. F., Diener A., Ebneth S., Godderis Y., Jasper T., Korte C., Pawellek F., Podlaha O. G., and Strauss H. (1999) $^{87}Sr/^{86}Sr$, $\delta^{13}C$ and $\delta^{18}O$ evolution of Phanerozoic seawater. *Chem. Geol.* **161,** 59–88.

Walker J. C. G. (1977) Evolution of the Atmosphere. New York, Macmillan.

Watson A., Lovelock J. E., and Margulis L. (1978) Methanogenesis, fires and the regulation of atmospheric oxygen. *Bio. Systems.* **10,** 293–298.