[AMERICAN JOURNAL OF SCIENCE, VOL. 289, April, 1989, P. 333–361]

A NEW MODEL FOR ATMOSPHERIC OXYGEN OVER PHANEROZOIC TIME

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ABSTRACT. A mathematical model has been constructed that enables calculation of the level of atmospheric O_2 over the past 570 my from rates of burial and weathering of organic carbon (C) and pyrite sulfur (S). Burial rates as a function of time are calculated from an assumed constant worldwide clastic sedimentation rate and the relative abundance, and C and S contents, of the three rock types: marine sandstones and shales, coal basin sediments, and other nonmarine clastics (red beds, arkoses). By our model, values of O_2 versus time, using a constant total sedimentation rate, agree with those for variable sedimentation rate derived from present-day rock abundances and estimates of erosional losses since deposition. This agreement is the result of our reliance on the idea that any increase in total worldwide sediment burial, with consequently faster burial of C and S and greater O_2 production, must be accompanied by a corresponding increase in erosion and increased exposure of C and S on the continents to O_2 consumption via weathering. It is the *redistribution* of sediment between the three different rock types, and not total sedimentation rate, that is important in O_2 control.

To add stability to the system, negative feedback against excessive O_2 fluctuation was provided in the modeling by the geologically reasonable assignment of higher weathering rates to younger rocks, resulting in rapid recycling of C and S. We did not use direct O_2 negative feedback on either weathering of C and S or burial of C because weathering rates are assumed to be limited by uplift and erosion, and the burial rate of C limited by the rate of sediment deposition. The latter assumption is the result of modern sediment studies which show that marine organic matter burial occurs mainly in oxygenated shallow water and is limited by the rate of supply of nutrients to the oceans by rivers.

Results of the modeling indicate that atmospheric O_2 probably has varied appreciably over Phanerozoic time. During the Late Carboniferous and Permian periods O_2 was higher than previously because of the rise of vascular land plants and the widespread burial of organic matter in vast coal swamps. A large decrease in O_2 during the Late Permian was due probably to the drying-up of the coal swamps and deposition of a large proportion of total sediment in C and S-free continental red beds. Sensitivity study shows that major parameters affecting results are the mean C concentration in coal basins and the relative sizes of the reservoirs of young (rapidly recycled) versus old rocks. Less sensitivity was found for changes over time in total land area undergoing weathering and the use of direct O_2 negative feedback on marine carbon burial. Good agreement for rates of C burial calculated via our model and via independent

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models, which are based on the use of stable carbon isotopes, indicates that the dominant factor that has brought about changes in atmospheric O_2 level (and the isotopic composition of dissolved inorganic carbon in seawater) over Phanerozoic time is sedimentation and not weathering or higher temperature phenomena such as basalt-seawater reaction.

INTRODUCTION

Oxygen gas, O_2, is present in today's atmosphere at a concentration of 20.9 percent. The most important long term processes affecting this concentration are O_2 production by the burial of organic matter in sediments, representing net worldwide photosynthesis over respiration, and the oxidative weathering of organic matter in sedimentary rocks (Holland, 1978, 1984; Walker, 1974; Garrels and Perry, 1974). Next in importance is the burial of sedimentary pyrite, FeS_2, and its oxidation during rock weathering (Berner, 1984). Other processes, such as the oxidation and reduction of iron (in minerals other than pyrite) and of manganese, and the oxidation of reduced volcanically and metamorphically derived gases, are of lesser importance (Holland, 1978). On the time scale of the past 600 my, representing the Phanerozoic, variation in the rates of burial and weathering of both organic matter and pyrite are likely, and because of the much shorter time of 5 to 10 my for the turnover of atmospheric oxygen, this should result in changes in the level of atmospheric oxygen. It is the purpose of this paper to try to document these changes.

It is possible to calculate values for atmospheric O_2 in the geological past if rates of burial and weathering of organic carbon and pyrite sulfur can be quantified as a function of time. This is because the burial and weathering reactions involve the production and consumption of O_2:

For organic matter:

$$CO_2 + H_2O \underset{\text{weathering}}{\overset{\text{burial}}{\rightleftharpoons}} CH_2O + O_2$$

For pyrite:

$$2Fe_2O_3 + 16Ca^{2+} + 16HCO_3^- + 8SO_4^{2-} \underset{\text{weathering}}{\overset{\text{burial}}{\rightleftharpoons}} 4FeS_2 + 16CaCO_3 + 8H_2O + 15O_2$$

Thus, for example, for each mole of pyrite sulfur buried, 15/8 moles of O_2 are produced.

Quantification of organic carbon and pyrite sulfur burial rates over time have until now been done almost exclusively through the use of isotopic data on the $^{34}S/^{32}S$ and $^{13}C/^{12}C$ of ancient oceans as recorded by sedimentary calcium sulfate and calcium carbonate respectively (Holser and Kaplan, 1966; Rees, 1970; Holland, 1973; Claypool and others,

1980; Schidlowski and Junge, 1981; Berner and Raiswell, 1983; Holland, 1984; Garrels and Lerman, 1984; Lasaga, Berner, and Garrels, 1985; Walker, 1986; Francois and Girard, 1986; Kump and Garrels, 1986; Berner, 1987). An exception is the work of Budyko, Ronov, and Yanshin (1987) where abundance data for organic carbon were used. Unfortunately Budyko and Ronov's study rests on some problematical assumptions. They are: (1) Organic matter, once buried, is not weathered again. Since there is no recycling, this necessitates unidirectional processes for the consumption of oxygen, such as the oxidation of primordial mantle-derived gases. (2) Present day absolute abundances of rocks are a direct measure of their original abundance. This neglects the greater loss of older rocks by erosion (and by magmatism and metamorphism). (3) Only organic carbon burial affects O_2 levels. This is erroneous as can be shown by the isotope models discussed above which demonstrate that at many times pyrite burial was an important source of atmospheric O_2. (4) The weathering uptake of O_2 by rocks is directly proportional to the level of atmospheric O_2. As shown below, this assumption is probably incorrect.

Here a new model for atmospheric O_2 is presented which rests on relative, rather than absolute, sedimentary rock abundance data and does not consider isotopic composition. In this way our study complements both the isotope studies of others and the work of Budyko and Ronov. Our reasoning is based partly on the study of modern environments. In the present ocean most burial of organic matter occurs in rapidly deposited near-shore sediments of deltas, shelves, estuaries, et cetera (Berner, 1982). Burial occurs under normal marine conditions which means in oxygenated bottom waters where bioturbating benthic organisms live. Rates of burial of organic matter and pyrite in such sediments are directly proportional to each other (Berner and Raiswell, 1983; Goldhaber and Kaplan, 1974) and to the rate of burial of total sediment. This relationship (fig. 1) demonstrates that organic carbon and pyrite sulfur concentrations in near-shore terrigenous sediments, on the average, fall within a limited range independent of sedimentation rate. Thus, carbon and sulfur burial rates directly track total sediment burial rate. The higher the worldwide sedimentation rate, the higher the rate of carbon and sulfur burial and the faster the production of O_2.

The direct proportionality between marine organic carbon burial and total sedimentation rate should not have been affected by changes in atmospheric O_2 levels in the geological past. Near-shore sedimentation occurs in waters that are in exchange equilibrium with the atmosphere and, therefore, has always occurred in the presence of oxygenated water during Phanerozoic time. (Based on the fossil record, one can be confident that at no time during the Phanerozoic has atmospheric oxygen been so low that shallow water marine life could not exist.) The rate of decomposition of organic matter in seawater is not a function of its O_2 content until very low O_2 levels are obtained (Devol, 1978; Berner,

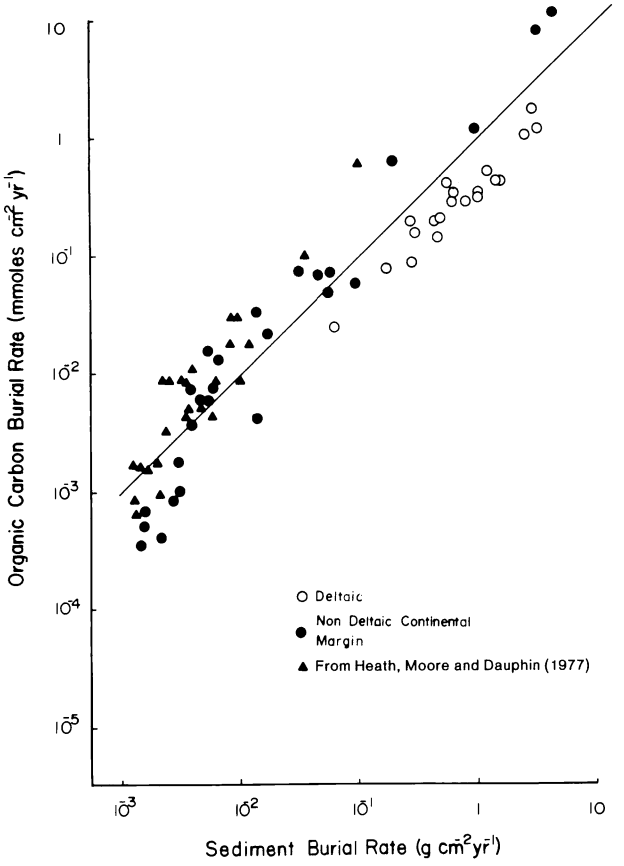

Fig. 1. Plots of organic carbon and pyrite sulfur burial rates versus total sediment burial rate for modern normal marine continental margin sediments. Data for sulfur burial are after the compilation of Canfield (ms), with additional data from Hartmann and others (1976). Data for carbon burial are from a number of sources: Westrich (1983), Canfield (ms), Martens and Klump (1984), Lyons and others (1980), Goldhaber and Kaplan (1980), Murray, Grundmanis, and Smethie (1978), Aller, Mackin, and Cox (1986), Shokes (1976), Filipek and Owen (1980), DeLuca Rebello and others (1986), and Hartmann and others (1976). The data of Heath, Moore, and Dauphin (1977) (down to a sedimentation rate of 10^{-3} g cm^{-2} yr^{-1}) are also shown.

1989). This is also true of oxic decomposition in sediments overlain by oxygenated bottom water. For example, Pamatmat and Banse (1969) found no dependence of sediment oxygen uptake on bottom water O_2 concentrations for shallow water stations in Puget Sound, USA, and for whole ocean basins, Smith and Hinga (1983) did not require an O_2 dependence to explain their data on O_2 sediment uptake. Thus, the key factor in organic matter and pyrite burial in shallow water sediments is sedimentation rate and not atmospheric O_2 level.

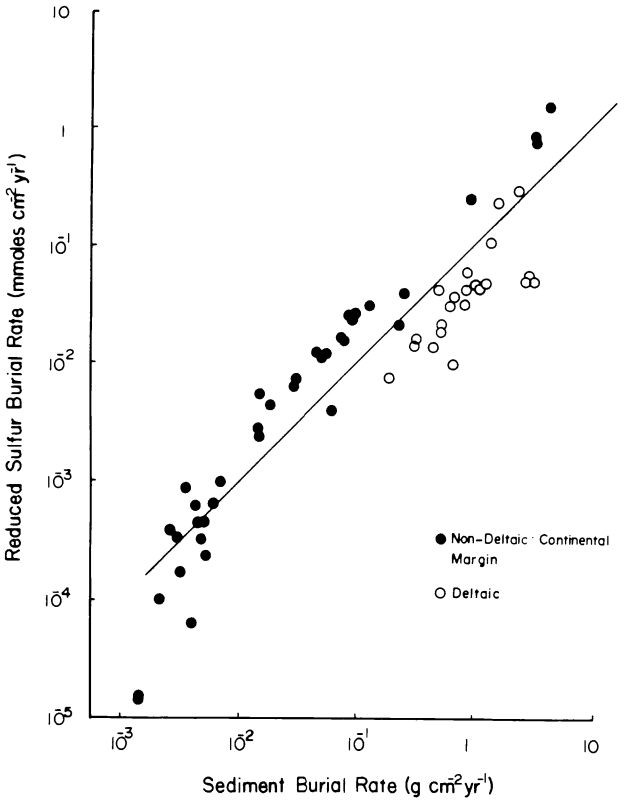

Fig. 1. (continued)

However, organic matter and pyrite burial in deeper ocean sediment may be affected by levels of atmospheric O_2. Suppose that, as a result of lower O_2 levels in the atmosphere, much greater portions of the deeper ocean became anoxic, a situation that may well have occurred during much of the early Paleozoic (Berry and Wilde, 1978; Wilde, 1987). Under such euxinic conditions (presence of H_2S and no O_2 in bottom waters along with a lack of bioturbation) more organic matter is preserved in sediments, which results in enhanced carbon burial (Demaison and Moore, 1980; Pratt, 1984; Canfield, 1989). Enhanced carbon burial, in turn, results in enhanced O_2 production which should act as a negative feedback limiting further increases in euxinicity. However, increased carbon burial can continue only as long as the nutrients phosphorus and nitrogen are available in the oceans. Once the nutrients are stripped from the sea, further organic production and burial are limited by the input of nutrients to the oceans by rivers (Holland, 1978; Broecker and Peng, 1982). No more organic burial can occur than is

permitted by the nutrient supply. At present rates of nutrient deposition, complete removal of nutrients would take considerably less than 1 my, a short time compared to that of the Phanerozoic or to the residence time of atmospheric O_2.

The above argument, of course, assumes that organic matter and nutrient burial are directly linked. If nutrients are also removed from seawater by competing processes, as is the case for phosphorus adsorption on ferric oxyhydroxides in modern deep-sea sediments (Berner, 1973; Sherwood, Sager, and Holland, 1987), then total organic burial may not be a simple function of riverine nutrient supply. In this case the spread of euxinicity could act as a negative feedback on atmospheric O_2 depletion by shifting phosphorus removal from adsorption on oxidized iron minerals to inclusion with organic matter. Such a shift would result in greater organic matter burial and greater O_2 production for a constant riverine nutrient input. Of course this could continue only up to the point where all supplied phosphorus is removed with organic matter, which for the modern oceans is about twice the amount presently removed (Froelich and others, 1982).

What has just been said concerning burial of organic matter in euxinic basins does not apply equally to pyrite burial. Euxinic sediments on average exhibit higher ratios of pyrite sulfur to organic carbon than do normal marine sediments because of the greater degree of pyrite formation under euxinic conditions (Berner and Raiswell, 1983; Raiswell and Berner, 1985: Canfield, ms). If, for constant total marine organic carbon burial, a large shift from normal marine to euxinic conditions occurred, then more pyrite sulfur would be buried worldwide. In other words, sulfur burial, as compared to carbon burial, is not controlled simply by nutrient availability.

If most burial of organic matter over time has occurred in nearshore sediments, then the major control on organic matter burial in the oceans is total sedimentation rate and not atmospheric O_2 level. In this case higher sedimentation rate means greater O_2 production most likely resulting in higher atmospheric O_2. To prevent a catastrophic O_2 increase (or decrease) there must be some negative feedback control. A major control is erosion (Kump, 1988; Berner, 1989). Higher sedimentation must mean higher erosion rates, and increased erosion means greater stripping of rock and exposure of old organic matter and pyrite to O_2 uptake via chemical weathering. Thus, sedimentation control of O_2 production entails an equivalent erosional control on O_2 consumption. Another feedback would be dependence of weathering uptake on atmospheric O_2 level. This is the basic assumption made by Budyko, Ronov, and Yanshin (1987). However, it is our belief, as well as that of others (Holland, 1978, 1984) that the rate-limiting step in the chemical weathering of pyrite and organic matter is uplift and exposure to weathering solutions and not the weathering reaction itself; in other words, the loss of atmospheric O_2 by the oxidation of reduced sulfur and carbon is controlled mainly by tectonism. This is because black and gray

shales, which contain most of the organic matter and pyrite, weather rapidly. If such shales are not constantly stripped of their weathered and oxidized soil mantle by erosion, the mantle can rapidly grow in thickness until it acts as a protective cap on the shales shielding the underlying unoxidized material from O_2-containing weathering solutions and, thus, inhibiting further oxidation.[1]

It might occur to the reader that equivalence of exposure of organic matter and pyrite by erosion and burial by sedimentation should, because of the short time of transport of sediment to the sea, provide a rapid oxygen feedback, thus allowing for little variation of O_2 with time. However, the rate of carbon and sulfur burial depends not only on how much sediment is deposited, but also on where the sediment is deposited. This is a most important concept of our model. Suppose that weathering and erosion of average sediments, containing a good proportion of organic-rich, pyrite-rich shales, is followed by sedimentation of most of the material on land as well-drained fluviatile deposits, such as red beds. These beds contain no organic matter or pyrite. The net result would be a draw-down of atmospheric oxygen, and this is a situation we believe occurred at the end of the Paleozoic. By contrast, erosion of oxidized continental clastics and deposition of the material in the sea along with organic matter and pyrite would bring about a rise in atmospheric O_2. It is the redistribution of sediment between organic-rich and organic-poor environments that we believe constitutes the principal control of O_2 variations over Phanerozoic time.

For the purposes of modeling we divide terrigenous sediments into three groups: marine clastics (sandstones and shales), coal-basin sediments, and continental clastics other than those deposited in coal basins (red beds, arkoses, variegated mudstones). Total worldwide deposition of organic carbon and pyrite sulfur depends then on the relative proportions of these three rock types, their reduced carbon and sulfur contents, and total sedimentation rate. Proportions of the three rock types can be calculated, for various times in the geologic past, from the rock abundance data of Ronov (1976) and Budyko, Ronov, and Yanshin (1987). Organic-rich lake sediments are neglected because of their rarity, and carbonates (limestones and dolostones) are assumed to be weathered and deposited at roughly equal rates over time thereby contributing nothing to O_2 fluctuations. (Since carbonates make up roughly only about 25 percent of total sedimentary rocks and contain

[1] What has been said about the tectonic control of weathering also applies to the breakdown of organic matter and pyrite during deep diagenesis, metamorphism, and magmatism, which are all tectonically regulated processes. This breakdown results in the release of reduced gases, mainly CH_4 and H_2S, which can make their way to the atmosphere and react with O_2. In this way the overall process of thermal breakdown and oxidation of reduced gases is analogous to weathering and is similarly controlled by worldwide tectonism. Thus, in the present study our rate expressions for weathering can be considered to include also, implicitly, lesser proportions of deep diagenesis, metamorphism, and volcanism.

little pyrite, variations in their burial rate should have only a minor effect on organic matter and pyrite burial anyway.)

To provide additional negative oxygen feedback in our modeling, we employ the concept of rapid recycling (Berner, 1987). The idea is that younger sediments have a higher probability of being weathered than older sediments. For example, organic-rich shelf sediments deposited during a high-stand of sealevel upon withdrawal of the sea are more likely to be weathered and oxidized than those buried beneath them or buried elsewhere. Likewise, fresh water peat is subjected to rapid weathering soon after its enclosing swamp is drained. In this way rapid rates of organic burial are followed soon thereafterward by rapid rates of organic weathering, and in this way a brake on atmospheric O_2 increases is provided. Rapid recycling requires the separation of older from younger sediments in modeling scenarios and necessitates greater mathematical complexity, but it is geologically reasonable and should be used wherever possible.

One aspect of our approach, as already mentioned above, is that nutrient supply is not always the dominant factor in organic matter and pyrite burial in marine sediments. For example, if most sediment deposition were to occur on land in low-organic red beds, nutrients would drain into the sea without accompanying mineral detritus. The nutrients would stimulate organic productivity, but without rapid burial, the organic matter would be re-oxidized, and nutrients would be liberated back to solution. This would result in a buildup of the inventory of oceanic nutrients. Such a buildup could not continue because there are a number of other mechanisms for removing nitrogen and phosphorus from the sea. In the case of nitrogen, denitrification to N_2 is always an important process for limiting the dissolved nitrate content of seawater (Söderlund and Rosswall, 1982). For phosphorus, removal with organic matter is less than half of total phosphorus removal in the present ocean (Froelich and others, 1982; Sherwood, Sager, and Holland, 1987). The remaining phosphorus is taken out in association with calcium carbonate (Froelich and others, 1982), adsorbed on ferric oxides and hydroxides (Berner, 1973; Sherwood, Sager, and Holland, 1987), and as phosphorite (Holland, 1978). In the geologic past, during periods when total marine sedimentation was less than today, the importance of these other nitrogen and phosphorus removal processes undoubtedly was greater.

METHOD OF CALCULATION

Sedimentological data.—As discussed above, we divide Phanerozoic sediments into three groups based on their reduced carbon and sulfur contents. They are: marine clastic sediments (shales and sandstones), coal basin sediments, and continental clastics other than those deposited in coal basins. These three rock groups account for about 80 percent of all preserved sedimentary rocks and an even higher percentage of earth surface organic matter and pyrite. Relative abundances of the three rock

types, as a function of geologic age, can be calculated from the data of Ronov (1976) to which we've added abundances of presently submerged shelf, rise, and deep-sea marine clastics of Jurassic-to-Recent age calculated from the data of Budyko, Ronov, and Yanshin (1987). Results are shown in table 1. Reduced carbon and sulfur contents for each rock type are estimated as follows. For marine clastics deposited since the mid-Devonian (about 380 my ago) a value of 0.6 percent organic carbon is used, based on the data of Raiswell and Berner (1986), Ronov (1976), Budyko, Ronov, and Yanshin (1987), and Holland (1978). For Cambrian to Devonian marine clastics a lower value of 0.4 percent carbon is used. This is based partly on the compilation of Ronov (1976) for sedimentary rocks of this age and partly on the assumption that prior to the advent of vascular land plants, the source of organic matter was restricted to marine organisms. All other factors being constant, burial of terrestrially-derived organic matter in marine sediments should result in higher contents of organic carbon because of the presence of bacterially refractory organic compounds derived from the lignin of vascular plants. Also, the higher carbon/phosphorus ratio of terrestrial organic debris (and coal), as compared to marine material (Meybeck, 1982),

TABLE 1

Distribution of clastic sediments among three major groups based on data of Ronov (1976) and Budyko, Ronov, and Yanshin (1987). Time scale that used by Ronov (1976) and by us in the present study

Period	Time Span (my BP)	% Marine Clastics	% Coal Basin Sediments	% Other Continental Clastics
Pliocene	2–9	74	2	24
Miocene	9–25	85	1	14
Oligocene	25–37	87	2	11
Eocene	37–58	89	3	8
Paleocene	58–66	80	3	17
Upper Cretaceous	66–100	81	5	14
Lower Cretaceous	100–132	78	3	19
Jurassic	132–185	75	4	21
Upper Triassic	185–210	50	1	49
Middle Triassic	210–220	77	1	22
Lower Triassic	220–235	55	0.5	44
Upper Permian	235–255	47	6	47
Lower Permian	255–280	61	10	29
Upper and Middle Carboniferous	280–320	58	22	20
Lower Carboniferous	320–345	74	8	18
Upper Devonian	345–360	74	0	26
Middle Devonian	360–376	82	0	18
Lower Devonian	376–400	76	0	24
Silurian	400–435	91	0	9
Ordovician	435–490	93	0	7
Upper Cambrian	490–515	95	0	5
Middle Cambrian	515–545	95	0	5
Lower Cambrian	545–570	93	0	7

means that for a given burial of phosphorus, more carbon is buried if the source is terrestrial plants (Kump and Garrels, 1986).

The average organic carbon content of coal basin sediments is not well known, but it can be restricted to the range of 0.5 to 5 percent carbon. This is based on: (1) the extensive compilation of the fractional thickness of coal basin sediments that are present as potentially mineable coals (Stutzer and Noé, 1940; International Geological Correlation Project Number 166, ms), (2) the average concentration of organic carbon in rocks other than coal in a number of coal basins computed from the data of Nicholls and Loring (1962), Eagar and Spears (1966), Pearson (1979), and R. Raiswell (personal commun.) (see also Berner, 1984), and (3) the average carbon content of coal and bulk density of coal and sedimentary rocks.

The organic carbon content of non-coal-containing continental clastics is essentially zero. This includes fluviatile sands and conglomerates, red beds, and variegated (red/green) shales and mudstones. Such sediments are deposited on well-drained slopes in which constant aeration results in the total destruction of organic matter (Van Houten, 1973).

The pyrite sulfur content of normal marine clastics is based on carbon/sulfur (C/S) ratios and the estimated organic carbon contents discussed above. (By normal marine we refer to sediments deposited in oxygenated bottom waters subject to bioturbation.) For modern fine-grained normal marine sediments the worldwide average C/S weight ratio is about 3 (Berner, 1982; Goldhaber and Kaplan, 1974; Volkov and Rozanov, 1983). This is assumed to represent the original burial value for all post-Devonian normal marine clastic rocks. Measured C/S ratios for post-Devonian normal marine shales are generally somewhat lower (Raiswell and Berner, 1986), but this can be attributed to preferential loss of organic carbon, relative to pyrite, during diagenesis (Raiswell and Berner, 1987). For Cambrian-Devonian sedimentary rocks an original C/S burial ratio of 2 is adopted for normal marine clastics. This is based on the measurements of Raiswell and Berner (1986) and Donnelly, Shergold, and Southgate (1988) corrected for the diagenetic loss of organic carbon. (Since we implicitly include within weathering the oxidation of reduced carbon and sulfur gases released to the surface from diagenesis, metamorphism, et cetera (see footnote, p. 339), the early diagenetic burial C/S value is the appropriate value to be used for long term burial.)

Organic carbon and pyrite sulfur are also buried in euxinic marine sediments, those deposited in anoxic bottom waters containing H_2S and devoid of bioturbating organisms. As discussed in the introduction, this results in sediments that exhibit, on average, lower C/S ratios than those in normal marine sediments. The quantitative abundance of euxinic sediments over Phanerozoic time is hard to estimate other than to say that there were certain periods when they were more abundant, such as during the early Paleozoic (see Berry and Wilde, 1978) and for

short periods during the Cretaceous (Arthur, Schlanger, and Jenkyns, 1987). Our approach is to assume that the relative abundance of euxinic vis-a-vis normal marine deposition is inversely proportional to the O_2 content of the atmosphere (see Wilde, 1987). This means that as O_2 decreases, the worldwide C/S ratio of marine sediments decreases, and the average reduced sulfur content of sediments, in general, increases. Mathematically this is equivalent to using calculated O_2 level as a negative feedback on pyrite sulfur burial and, thus, O_2 production. Also, to cover the situation of a possible shift in phosphorus burial from oxidized to reduced, or euxinic conditions, as discussed earlier, we employ in some of our calculations an inverse proportionality between atmospheric O_2 level and both organic carbon and pyrite sulfur burial, but only for marine sediments. Carbon burial in coal basins should be independent of atmospheric oxygen because coal swamp development is largely a climatic and topographic phenomenon.

The pyrite sulfur content of both coal basin and non-coal bearing continental clastics is assumed to be zero. This is substantiated by the very high C/S ratio of coal and non-marine shales (Berner, 1984) and the absence of both organic carbon and pyrite sulfur in arkoses, red beds, et cetera.

The model.—Burial of organic carbon and pyrite sulfur, at any given time in the past, is given by the expressions:

$$F_{BC} = (1/12)[(\%C_{MA})(f_{MA}) + (\%C_{CB})(f_{CB})]F_T \quad (1)$$

$$F_{BS} = (1/32)[O_2(0)/O_2(t)](\%S_{MA})(f_{MA})F_T \quad (2)$$

where:

F_{BC}, F_{BS} = worldwide burial rate of organic carbon (C) and pyrite sulfur (S) (in 10^{18} moles per million years)

f_{MA}, f_{CB} = fraction of total clastics present as marine clastics (MA) and coal basin sediments (CB) respectively (values of table 1 divided by 100)

F_T = worldwide burial rate of total clastic sediments (in 10^{20} g per million years)

$\%C_{MA}$, $\%C_{CB}$ = average percent organic carbon in marine clastics and coal basin sediments respectively

$\%S_{MA}$ = average percent pyrite sulfur in normal marine sediments

$O_2(0)/O_2(t)$ = ratio of number of moles of O_2 in the present atmosphere ($t = 0$) to the number of moles at a given time t

1/12, 1/32 = stoichiometric ratios for converting grams to moles

(To test the sensitivity of our model to the use of O_2 feedback on marine organic carbon burial, we also multiply the first term within the brackets on the right of eq (1) by $[O_2(0)/O_2(t)]$).

Weathering of organic carbon and pyrite sulfur, as discussed in the introduction, is assumed not to respond to changing atmospheric O_2 levels but rather to changing worldwide erosion rates equivalent to

changing worldwide sedimentation rates. The appropriate expressions are:

$$F_{WC} = |F_T(t)/F_T(0)|k_W C_T \quad (3)$$

$$F_{WS} = |F_T(t)/F_T(0)|k_W S_T \quad (4)$$

where:

F_{WC}, F_{WS} = worldwide weathering rates of organic carbon (C) and pyrite sulfur (S) in 10^{18} moles per million years
$F_T(t)$, $F_T(0)$ = worldwide total clastic burial rate at time t and at present (t = 0)
C_T, S_T = total masses of organic carbon and pyrite sulfur, respectively, in sedimentary rocks (in 10^{18} moles)
k_W = weathering rate constant

These equations express the viewpoint that the weathering rate constants for organic carbon and for pyrite sulfur are the same. This is reasonable in that reduced carbon and reduced sulfur are almost always present together and can be removed from a rock (usually a shale) and oxidized only by the complete breakdown of the rock. The equations are also based on the assumption that the weathering rate constant for marine clastics and coal basin sediments are similar, so that all organic carbon can be lumped into one reservoir rather than being distributed between two reservoirs (marine and coal basin), each with its own weathering rate constant. In this way our weathering expressions are similar to those used in isotope modeling (Garrels and Lerman, 1984). Values of k were derived from present day weathering fluxes divided by their respective present day masses (Garrels and Lerman, 1984) but with the modification that k values for organic matter and pyrite were assumed to be the same as discussed above.

In actual practice eqs (3) and (4) were not used except for preliminary exploration of the model. Instead, to provide negative feedback to the system, and, thus, reduce O_2 fluctuations, the rapid recycling approach (Berner, 1987) was applied to weathering. As discussed earlier, this method rests on the geologically reasonable idea that younger sediments are more likely to undergo weathering than older rocks. In order to effectuate rapid recycling, the organic carbon and pyrite sulfur reservoirs were divided into young and old sub-reservoirs, and the young reservoirs were assigned weathering rate constants much higher than the old reservoirs. This necessitates much smaller sizes for the young reservoirs in order to maintain the same total weathering fluxes calculated by the simple (non-rapid recycling) model.

The rapid recycling model is diagrammatically illustrated in figure 2, and the appropriate weathering expressions are:

$$F_{WCY} = |F_T(t)/F_T(0)|k_{WY} C_{TY} \quad (5)$$

$$F_{WCO} = |F_T(t)/F_T(0)|k_{WO}\, C_{TO} \quad (6)$$

$$F_{WSY} = [F_T(t)/F_T(0)]k_{WY}S_{TY} \quad (7)$$

$$F_{WSO} = [F_T(t)/F_T(0)]k_{WO}S_{TO} \quad (8)$$

$$F_{WC} \equiv F_{WCY} + F_{WCO} \qquad F_{WS} \equiv F_{WSY} + F_{WSO}$$

where:

k_{WY}, k_{WO} = weathering rate constants for the young (Y) and old (O) reservoirs respectively

F_{WCY}, F_{WCO}, C_{TY}, C_{TO} = weathering fluxes and masses of total organic carbon in the young and old reservoirs respectively

F_{WSY}, F_{WSO}, S_{TY}, S_{TO} = weathering fluxes and masses of pyrite sulfur in the young and old reservoirs respectively,

and other symbols are as defined above. Note that again it is assumed that coal basin sediments and marine clastics weather at the same rate and that one can have both young and old coal basin rocks undergoing weathering as well as young and old marine sediments. Also, it is assumed that the old reservoirs maintain constant mass (Berner, 1987). This means that there are aging fluxes F_{YOC}, F_{YOS} for carbon and sulfur equal to the constant weathering flux for each of the old reservoirs. This is also shown in figure 2.

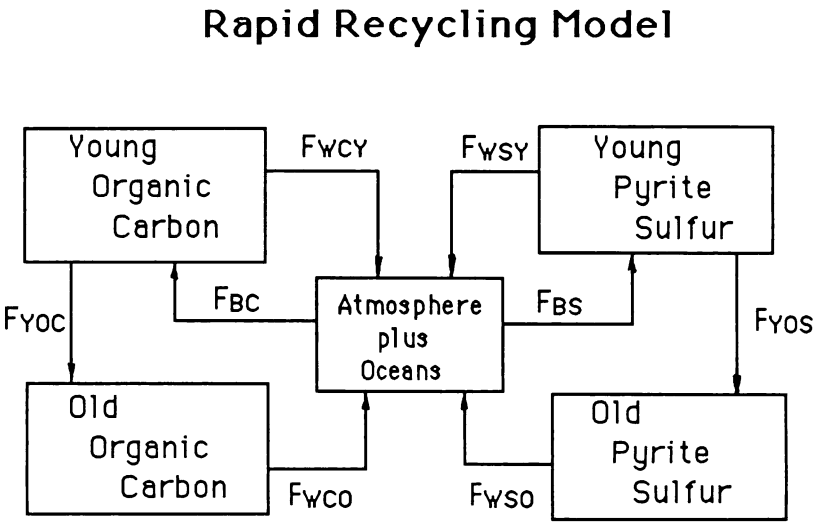

Fig. 2. Diagrammatic representation of the rapid recycling model of the present study. Some initial values (equal to present values) used in the modeling: mass of total organic carbon (young plus old reservoirs) 1250×10^{18} moles; mass of total pyrite sulfur 167×10^{18} moles; present mass of atmospheric O_2 38×10^{18} moles; present total weathering fluxes (young plus old) for organic carbon, 5.0×10^{18} mol/my and for pyrite sulfur, 0.67×10^{18} mol/my; present total sediment deposition rate, 130×10^{20} g/my.

The expression for atmospheric O_2 level, following the stoichiometry of the two reactions presented in the introduction, is:

$$dO_2/dt = F_{BC} + (15/8)F_{BS} - [F_{WC} + (15/8)F_{WS}] \quad (9)$$

where:

O_2 = atmospheric O_2 content (in 10^{18} moles)
t = time

Thus, by substitution of the appropriate values of F_{BC}, F_{BS}, F_{WC}, F_{WS} as a function of time in eq (9) and use of an initial O_2 value, one can calculate O_2 levels over Phanerozoic time.

Calculation was done by assuming an initial value for O_2 and solving eqs (1), (2), (5), (6), (7), (8), and (9) and computing new values for the masses of carbon and sulfur in each young reservoir:

$$C_{TY}(t) = C_{TY}(t - 1) + F_{BC} - F_{WCY} - F_{YOC}$$

$$S_{TY}(t) = S_{TY}(t - 1) + F_{BS} - F_{WSY} - F_{YOS}$$

(Recall that the masses of carbon and sulfur in the old reservoirs were assumed constant with time.) The new young reservoir values were then used, at the next time step, to generate new flux values and so forth. A time step of 1 my was found to be sufficient for convergence. Interpolated values were derived by graphing the data of table 1.

For values of F_T we used sediment burial values computed by W. S. Hay (personal commun. to R. Oglesby) who applied erosional loss corrections to the present day sedimentary rock abundance data of Ronov (1976). Unfortunately this approach is subject to a variety of possible errors related to estimates of absolute rock abundance and of losses by erosion. However, it turns out that knowledge of accurate values of F_T is not important because use of a constant value of $F_T = F_T(0)$ gives results for O_2 versus time very similar to those using the F_T values calculated by Hay.

For the sake of completeness we also did a computer run incorporating the effects of changing continental land area on weathering. The work of Berner, Lasaga, and Garrels (1983) emphasizes the significance of land area in modifying the worldwide weathering of all rocks. For this purpose we multiplied each weathering rate expression by the ratio A(t)/A(0), where A refers to total continental land area and 0 to today (also 570 my ago—see below). Data on land area versus time A(t) published by Ronov (1976) were used in this calculation.

We found that running the program backward starting with present conditions resulted in unacceptable mathematical instability. Therefore, we were forced to run forward, starting at 570 my BP, and to adopt an initial condition that would allow recovery of present conditions at the end of each run. Through trial and error we found that recovery of present day values for the masses of organic carbon, pyrite sulfur, and atmospheric oxygen were best obtained if we started with

present-day values at the beginning of the Cambrian. (Sensitivity to initial O_2 level, however, was generally small because of the much smaller size of the O_2 reservoir compared to those for total organic carbon and pyrite sulfur.)

RESULTS

Plots of atmospheric O_2, organic carbon burial rate, and pyrite sulfur burial rate versus time are shown in figures 3 to 13. Sensitivity to the use of constant versus variable worldwide sedimentation rate is shown in figures 3 and 4. Sensitivity of O_2 versus time to different values of the organic carbon concentration in coal basin sediments is shown in figure 5, and sensitivity to changes in the relative sizes and weathering rates of the young and old reservoirs is shown in figures 6 and 7. Our "best" estimate of carbon burial rate is compared to that derived from stable isotope modeling in figures 8 and 9. For the latter we recalculated values, using the rapid recycling approach (Berner, 1987) and young

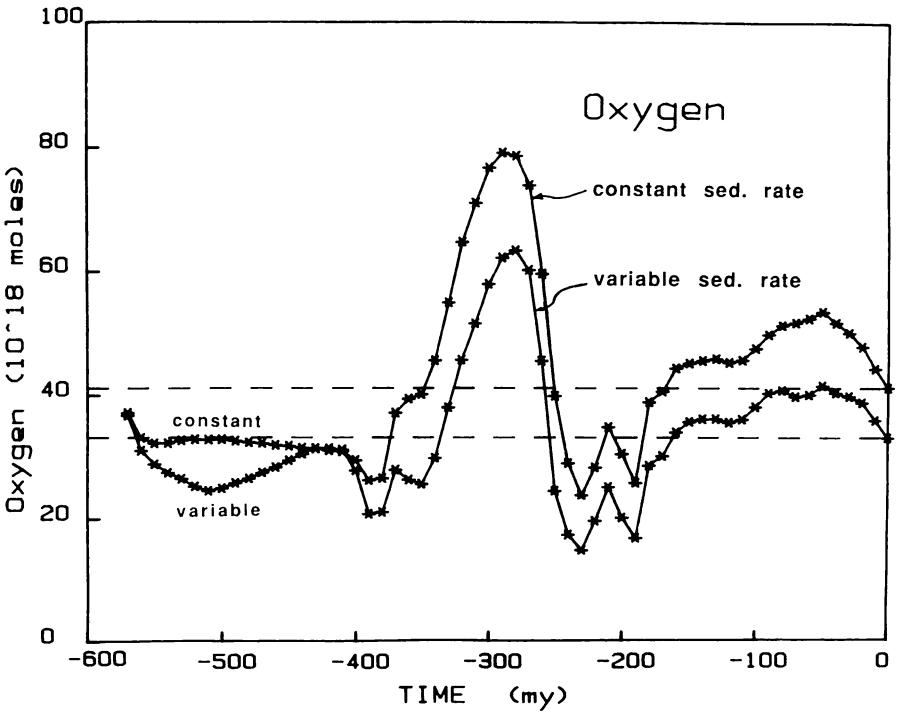

Fig. 3. Atmospheric oxygen versus time for constant and variable worldwide total sedimentation rates. Variable sedimentation rates taken from unpublished calculations of W. Hay based on the data of Ronov (1976). Results for 2.5 percent organic carbon in coal basins and a mean residence time of the young reservoirs, relative to conversion to old reservoirs, of 100 my.

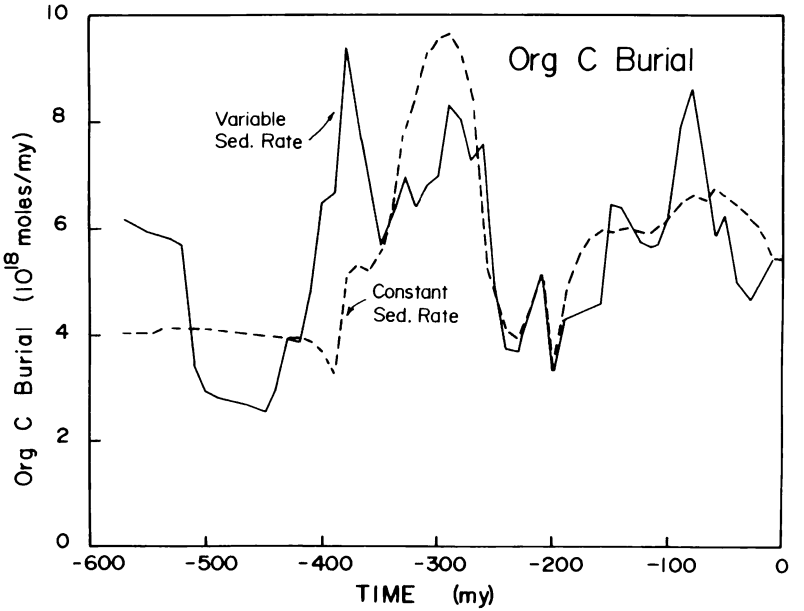

Fig. 4. Organic carbon burial rate versus time for constant and variable total sedimentation rates (same conditions as for fig. 3).

and old reservoir sizes and weathering rates identical to those used to obtain figure 8. In figure 10 is shown our estimate for pyrite sulfur burial based on the same parameters used to obtain the data of figure 9. (Comparison with isotope modeling for oxygen-feedback-modulated pyrite burial under the same recycling conditions was impossible because of complications introduced to isotope models when oxygen feedback is employed—see Berner, 1987). In figure 11 is shown the result obtained for O_2 versus time when the effects of varying land area are included. In figure 12 is shown the effects of using negative O_2 feedback for the burial of both organic carbon and pyrite sulfur in marine sediments. In figure 13 is shown our "best" estimate of atmospheric O_2 versus time including estimated errors.

DISCUSSION

As can be seen from figure 3 there is reasonably good agreement between O_2 values calculated on the basis of constant worldwide sedimentation rate and variable sedimentation rate with time. The main reason for this agreement is that variations in sedimentation rate are employed in expressions both for weathering and burial (see eqs 1–4). This is important and shows that the total sedimentation-erosion feedback mechanism is highly effective in stabilizing atmospheric oxygen.

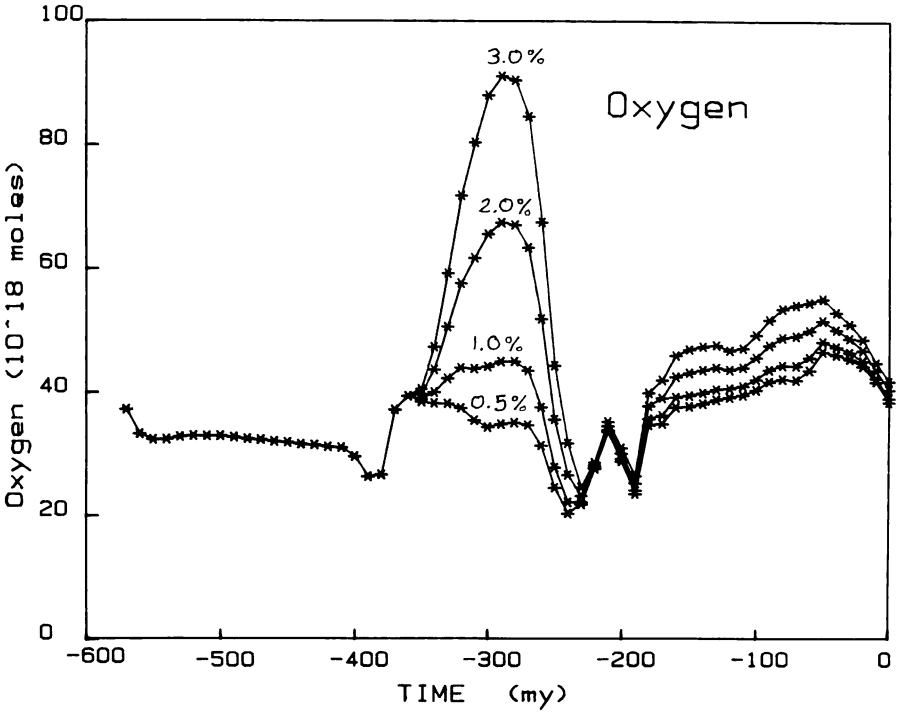

Fig. 5. Atmospheric oxygen versus time for different mean organic carbon concentrations in coal basin sediments (coal plus disseminated carbon). Mean residence time of young reservoirs, relative to conversion to old reservoirs, of 100 my; constant total sedimentation rate of 130×10^{20} g/my.

(This is also true for nutrients. Greater erosion means greater liberation of phosphorus, for example, to solution and, thus, greater supply of phosphorus for greater burial of marine and non-marine organic matter.) Of course, burial rates for organic matter appear very different when comparing results for constant sedimentation versus variable sedimentation (see fig. 4). However, because of the many assumptions about absolute rock abundances that go into the calculation of changing total sedimentation rates (see Gregor, 1985), we feel that the assumption of constant sedimentation rate gives better results. Also, with constant total sedimentation rate our results for organic matter burial are in much better agreement with the independent results of isotope modeling. This is shown in figures 8 and 9. This agreement gives some credence to our belief that worldwide total sedimentation rate has not changed greatly over Phanerozoic time. It is the location of this sedimentation that is important, not the amount. More importantly, agreement between results for isotope modeling and the results of the

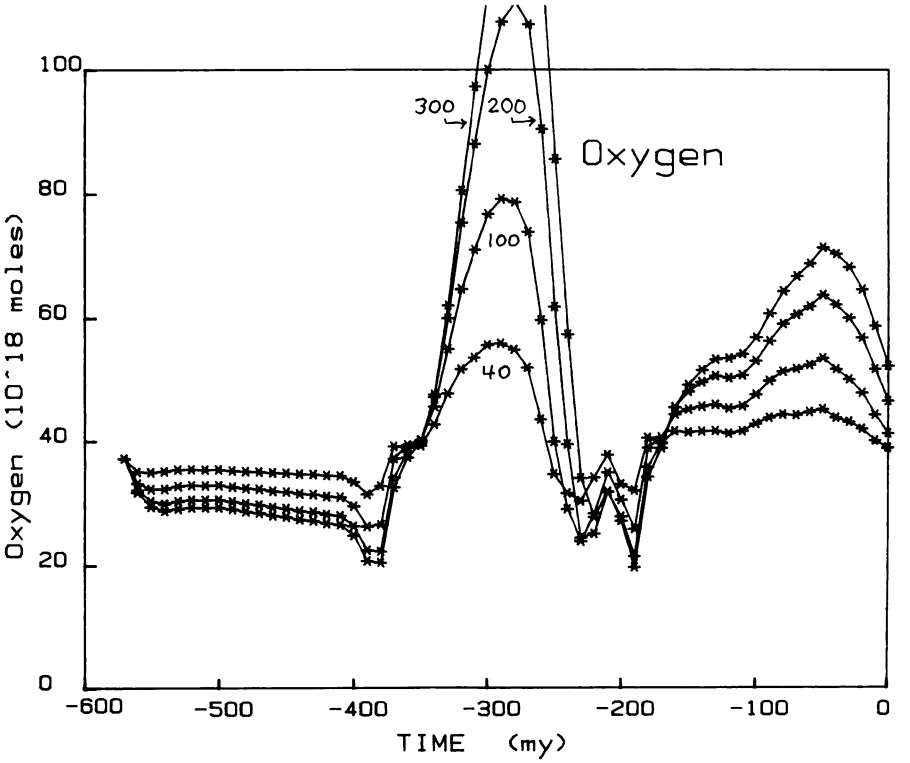

Fig. 6. Atmospheric oxygen versus time for different mean residence times of young reservoirs (in millions of years) relative to conversion to old reservoirs. Calculated for 2.5 percent organic carbon in coal basins; constant total sedimentation rate.

present study reinforces the idea that organic matter burial over Phanerozoic time was the major control on the isotopic composition of dissolved inorganic carbon in the oceans. Furthermore, essential correspondence between our curve for pyrite sulfur burial (fig. 10) and the value of $\delta^{34}S$ for seawater (Claypool and others, 1980) provides additional evidence for the importance of sediment burial on oceanic isotopic composition.

Figure 5 shows that burial of organic matter as coal and associated organic matter-containing non-marine sediments is an important process affecting atmospheric O_2 burial during the Permian and Carboniferous. The burial rate of organic matter in coal basins should not be affected by the level of atmospheric O_2, because coal swamps are predominantly a climatological and topographic phenomenon. Thus, our assumption of no O_2 feedback on organic matter discussed earlier is appropriate for terrestrial as well as near-shore marine sediments. The

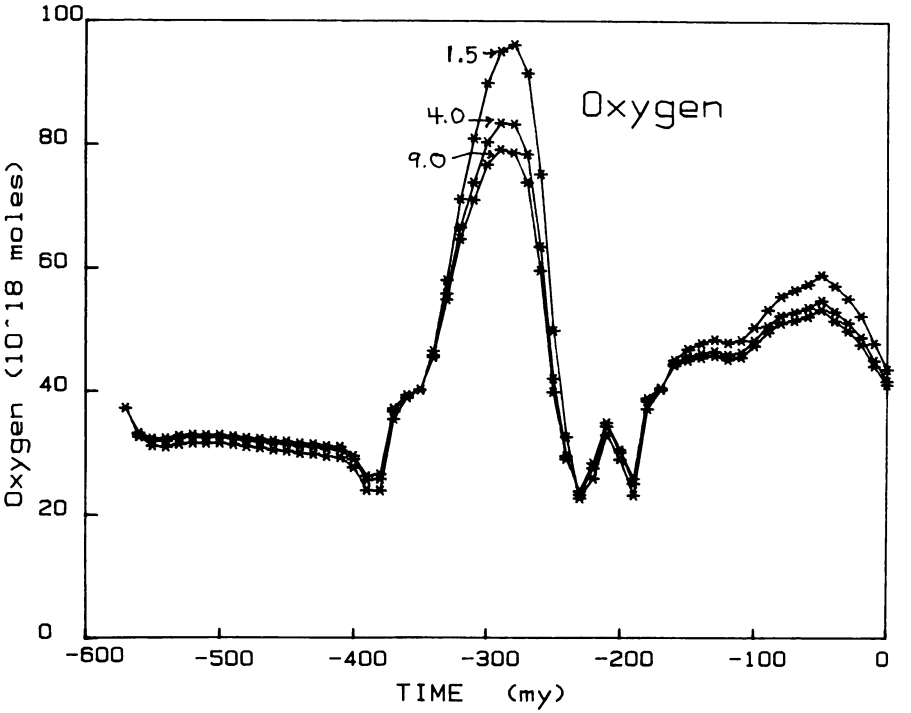

Fig. 7. Atmospheric oxygen versus time for different ratios of weathering fluxes for young versus old reservoirs (F_{WCV}/F_{WCO}; F_{WSV}/F_{WSO}). Calculated for 2.5 percent organic carbon in coal basins, a constant ratio of relative sizes of old/young reservoirs of 24, and constant total sedimentation rate.

average percent organic carbon in coal basins is not well known, but the multitude of data on the abundance of economic deposits of coal, to which is added the amounts of non-economic organic carbon, indicate values within the range shown in figure 5. Our best guess is an average value of about 2.5 percent carbon. This gives an oxygen maximum during the Upper Carboniferous of about twice the present O_2 level.

Sensitivity to variations in the organic content of marine clastics has been considered but is not shown here. For each of the pre-Carboniferous time periods shown in table 1, Ronov (1976) shows a variation of ±50 percent around the mean value for organic carbon contents of sedimentary rocks (marine plus non-marine) deposited over Cambrian-Devonian time. Since sediments in this age range are almost entirely marine (table 1), it is reasonable to assume the same variation for marine rocks of this age. For the time range Jurassic-to-Recent, one can calculate from the data given by Budyko, Ronov, and Yanshin (1987) that period-to-period variations are also about ±50 percent

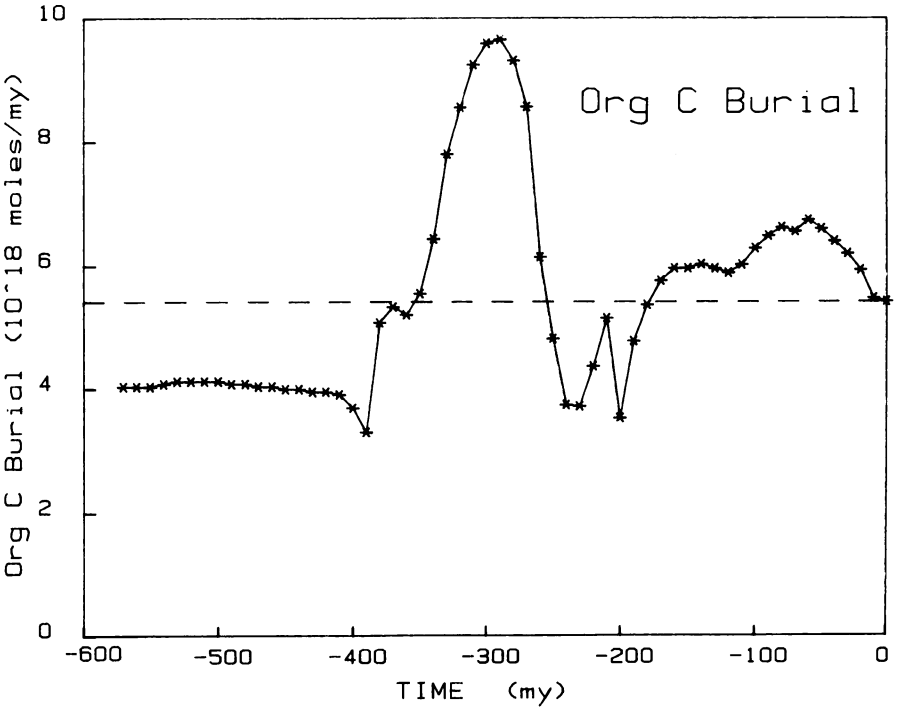

Fig. 8. "Best" values for organic carbon burial rate versus time for 2.5 percent organic carbon in coal basins, a mean residence time for the young reservoirs, relative to conversion to the old reservoirs, of 100 my, and constant total sedimentation rate.

around the mean post-Jurassic value. Variations of ±50 percent do not seriously alter the overall trend shown in figures 4 and 8 for rates of organic carbon burial, especially since errors in estimating average carbon contents for different periods can be as high as ±50 percent. (The carbon contents, as a function of age, for each of the three different rock types of the present study are not given in the Ronov and Budyko compilations; therefore, we had to estimate these values independently.) One might play the "devil's advocate" and try to lower the Permo-Carboniferous peak in figures 4 and 8 by assuming a much lower carbon burial in marine sediments at this time in order to balance the increased carbon burial in coal basins. However, this does not work. First, in order to flatten the Permo-Carboniferous peak, the mean content of organic matter in Permo-Carboniferous marine sediments, using the data in table 1, would have to be lowered from 0.6 percent to less than 0.1 percent. This is excessive. Furthermore, the burial of coal and associated non-marine organic matter involves very little phosphorus burial judging from the very high C/P value of coals (Stutzer and

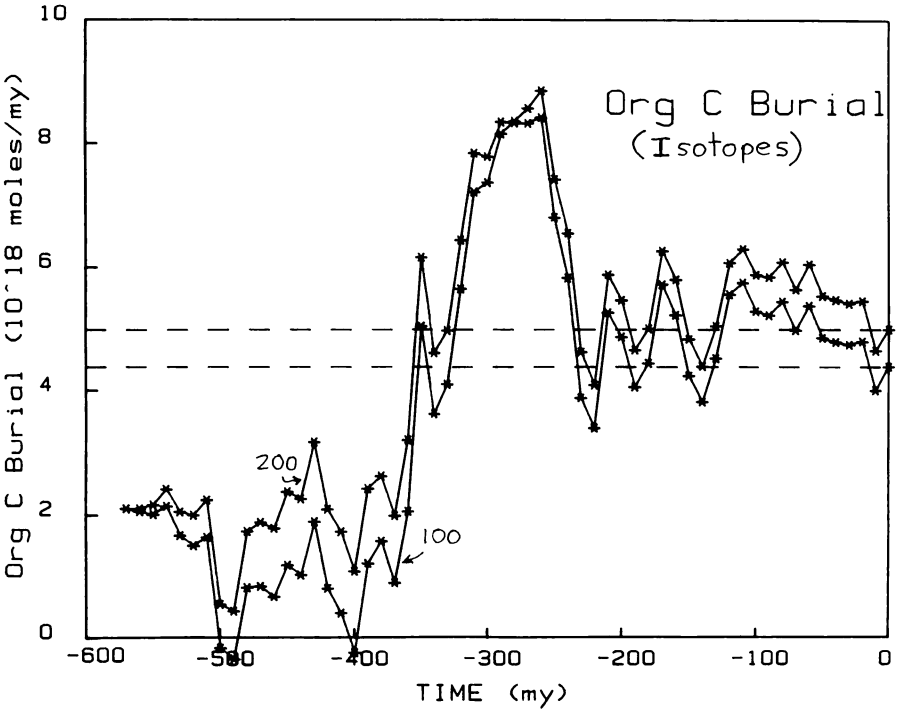

Fig. 9. Values of organic carbon burial rate versus time calculated by the rapid recyling model for carbon and sulfur isotope mass balance (see Berner, 1987). Numbers on graph refer to mean residence times (in millions of years) for the young reservoirs, relative to conversion to the old reservoirs. Compare with figure 8.

Noé, 1940). As a result, increased non-marine organic carbon burial does not simply mean the robbing of appreciable nutrients that would otherwise be delivered to the oceans by rivers and, thus, does not necessitate a concomitant lowering of marine organic carbon burial.

Sensitivity of O_2 versus time plots to changes in the relative sizes and weathering rates of the young and old reservoirs (figs. 6 and 7) is considerable. Based on the present-day distribution of sedimentary rock ages on the continents, we feel that the best choice of young reservoir size is that which gives a mean age, relative to conversion to old material (F_{YOC}, F_{YOS}; fig. 2) of 50 to 100 my. (In our runs the aging fluxes F_{YOC}, F_{YOS} are held constant while the mass of carbon and sulfur in the young reservoirs changes as a result of differences in burial rate and weathering rate. Thus, the aging residence time, defined as mass divided by aging flux, varies. The appropriate average value for the aging residence time is denoted here as the "mean age relative to conversion to old material.") Most of the actively eroding sedimentary rocks exposed

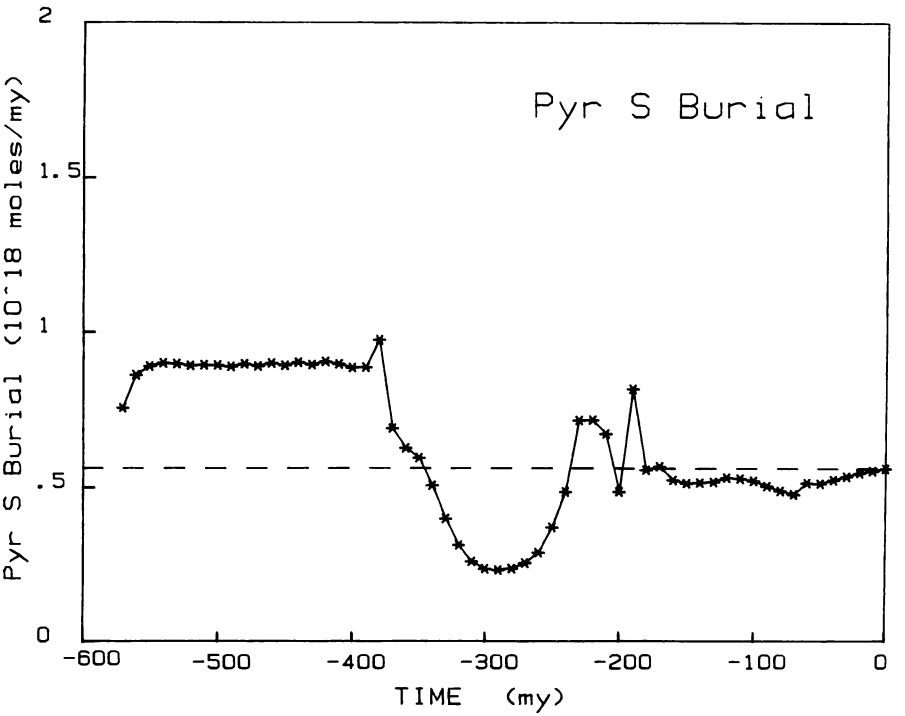

Fig. 10. Values for pyrite sulfur burial rate versus time for the same conditions listed for figure 8.

at the surface of the Earth today fall within this range; in other words, rocks undergoing the most active weathering are generally less than 100 my old. Note that there is less sensitivity to relative weathering rates than to aging residence times (compare figs. 6 and 7). Our investigated range in the ratio of weathering fluxes, F_{WCY}/F_{WCO} and F_{WSY}/F_{WSO} is between 1.5 and 9. Because of large differences in reservoir size, this means that the weathering constants k_W for the young reservoirs are on the order of ten to one hundred times higher than for the old reservoirs. In other words, there is a ten-fold to hundred-fold higher probability of weathering a "young" rock, by our model, than an "old" rock.

Our adopted values also mean that the mean age of the young carbon and sulfur reservoirs, relative to weathering (weathering residence time expressed as k_w^{-1}), ranges from about 10 to 30 my. These are reasonable values for the exposure and covering over by the sea of shallow water sediments due to fluctuations in sealevel or uplift accompanying local tectonics. Appreciable variations in sealevel on this general time scale have been well documented (Vail, Mitchum, and Thomp-

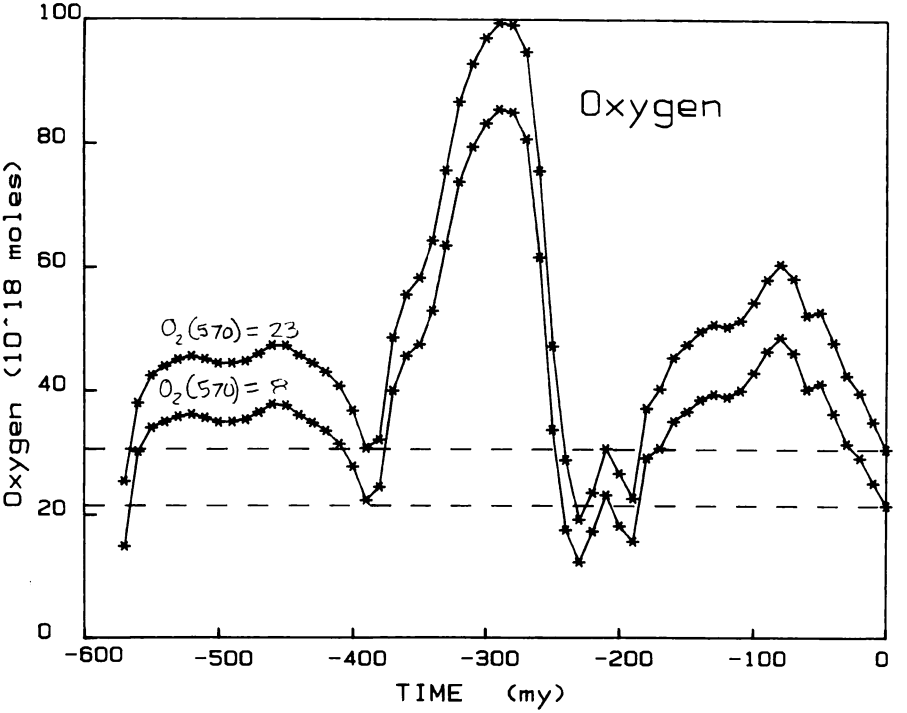

Fig. 11 Values of atmospheric oxygen versus time with inclusion of the effects of varying total continental land area. Otherwise same conditions as in figure 8. (Continental land area from the data of Ronov, 1976.) Note sensitivity to initial O_2 levels.

son, 1977) and correlate with the timing of major subareal exposures of sedimentary rocks (Esteban and Klappa, 1983). It should be remembered that sealevel fluctuations should not only bring about the exposure of marine sediments to weathering but also the subjection of coal basin sediments to weathering and erosion. Most coals are deposited in lowland swamps close to sealevel so that a lowering of sealevel, or baselevel, would bring about drainage of the swamps, erosion of the coal-swamp deposits, and therefore, enhanced exposure to oxidative weathering. Such a scenario of sealevel lowering and enhanced coal weathering actually has been postulated by Holser and Margaritz (1987) to have taken place at the end of the Permian period.

Finally, perusal of figure 11 shows that including land area in the calculation of O_2 versus time gives results not qualitatively different from those that ignore land area (compare figs. 11 and 13. Two curves are shown in figure 11 to illustrate the effects of varying initial O_2 content.) Also, in figure 12 is shown the effect of including O_2 negative feedback on both organic carbon and pyrite sulfur burial in marine

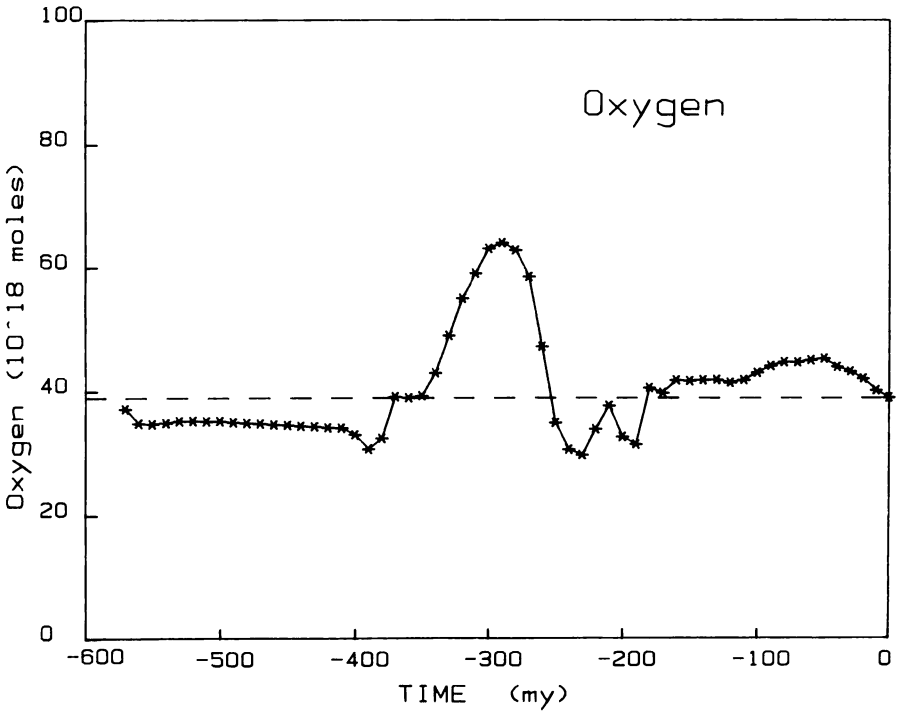

Fig. 12. Values of atmospheric oxygen versus time with inclusion of O_2 negative feedback for both organic carbon and pyrite sulfur burial in marine sediments. This reflects the situation when oceanic nutrient removal is partly independent of organic matter burial. Otherwise same conditions as in figure 8.

sediments. Although there is some dampening of fluctuations in O_2, compared with figure 13, again there is no appreciable qualitative effect. These plots, thus, further illustrate the robustness of our model.

ATMOSPHERIC OXYGEN OVER PHANEROZOIC TIME

Our "best" estimate of O_2 versus time is shown in figure 13. (The reader is cautioned that, because of sensitivity to values chosen for the organic C content of coal basins and recycling rates, amongst other things, this plot is really only an estimate and should be viewed in a qualitative to semi-quantitative manner.) The most outstanding feature of this plot is the large rise in O_2 in the Late Devonian-Carboniferous and its rapid plunge at the end of the Permian. A major reason for the Carboniferous increase in O_2 is the enhanced burial of organic carbon acompanying the rise of vascular land plants (Holland, 1978; Berner and Raiswell, 1983; Berner, 1987; Kump, 1989). The presence of vascular plants provided a new source of organic matter that was previously restricted only to marine organisms. The plants provided compounds,

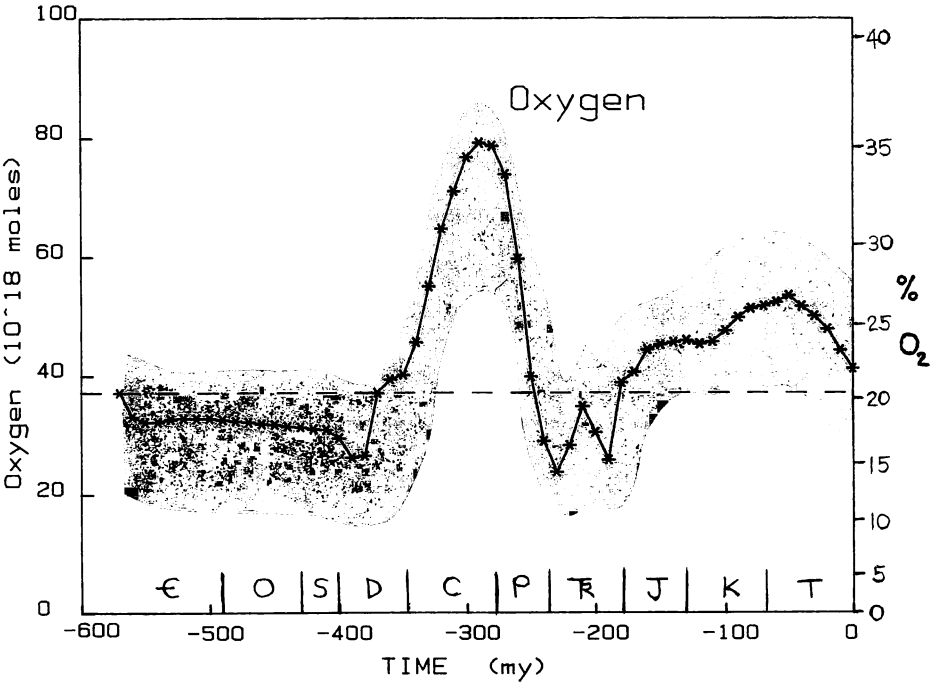

Fig. 13. "Best estimate" of atmospheric oxygen versus time from the present study for the same conditions listed for figure 8 (constant total land area). The values of O_2 shown here should be considered in only a qualitative-to-semi-quantitative sense. For this reason a crude (shaded) error zone, based on our sensitivity analysis, is included. Dashed line represents present atmospheric value. Time scale from Ronov (1976).

such as lignin-derived and humic substances, that could be preserved in sediments because of their greater resistance to bacterial decay than marine-derived material (Tissot and Welte, 1984; Lyons and Gaudette, 1979). This lignin-derived material could be deposited both on land, in coal swamps, and in the sea after being carried there by rivers. In addition, the carbon/phosphorus ratio of coal (Stutzer and Noé, 1940) and of vascular plant-derived organic matter (Meybeck, 1982) is higher than that for marine organic matter, so that for a given worldwide rate of burial of organic phosphorus, more carbon would be buried if an appreciable proportion of the organic matter were derived from land plants (Kump and Garrels, 1986).

Another cause for enhanced carbon burial during the Carboniferous and early Permian is the presence of vast lowland swamps at that time where the vascular plant material could be preserved to form coals and coaly shales. The abundance of flooded lowlands may well have been due to the emergent nature of the supercontinent of Pangea at that time, but it also must have been due to climatic circumstances.

A change in climate to more arid conditions (see Tardy, N'Kounkou, and Probst, this issue, p. 455) probably best explains the rapid lowering of O_2 at the end of the Permian Period. At this time deposition of continental clastics in organic-rich coal swamps was replaced by deposition in well-drained regions to form red beds, variegated shales, et cetera. In addition, there was a pronounced drop in sealevel at the very end of the Permian exposing the previously deposited Carboniferous and Permian coals to enhanced uptake of O_2 by erosion and weathering (Holser and Magaritz, 1987). This sealevel drop may well have been a major cause of the drop in O_2, but climatic drying probably also played a major role. At any rate, our modeling indicates a major drop in O_2 at this time, and this is the most pronounced feature for all of Phanerozoic time.

Our modeling suggests that distinctly higher atmospheric O_2 levels than at present existed during the Permo-Carboniferous and (to a lesser extent) the Cretaceous-Early Tertiary and that lower levels occurred during the Triassic and possibly during the early Paleozoic. Is this reasonable? There are a number of studies that have also concluded that atmospheric O_2 must have changed over Phanerozoic time (Tappan, 1968; Walker, 1974; Holland, 1978, 1984; Kump and Garrels, 1986; Shackleton, 1985; Lasaga, Berner, and Garrels, 1985; Berner, 1987; Budyko, Ronov, and Yanshin, 1987; Holser and Magaritz, 1987; Arthur, Schlanger, and Jenkyns, 1987), but there are no simple indicators of O_2 levels to turn to for the Phanerozoic. (Preliminary results on gases trapped in amber suggest higher O_2 levels during the Cretaceous, but this method requires much more testing—see Berner and Landis, 1988). The possible range of O_2 can be constrained by the increased susceptibility of trees to forest fires at elevated O_2 levels (Watson, Lovelock, and Margulis, 1978; Kump, 1988), but much more work in this area is needed to obtain a firm upper limit. Certainly at higher O_2 levels one might expect more forest fires, and evidence for this may exist in the abundance of fossil charcoal (Cope and Chaloner, 1985). Additional evidence for fluctuating O_2 levels, from the deduced paleophysiology of fossil organisms or paleoecology of plants, has not yet been adequately studied. It is hoped that the present study will help to focus others on investigating the possibility that atmospheric oxygen levels have changed over Phanerozoic time and that such paleontological studies as that of McAlester (1970) can be built upon and expanded.

ACKNOWLEDGMENTS

We thank Lee Kump and H. D. Holland for helpful reviews of the manuscript. We also acknowledge the inspiration of R. M. Garrels and of Sir Charles Lyell who said (Principles of Geology, tenth Edition, 1867, p. 107) ". . . deposition and denudation are processes inseparably connected, and what is true of the rate of one of them, must be true for the rate of the other. . . ." Research supported by NSF Grants OCE 8508472 and EAR 8617600.

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