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MODELS FOR CARBON AND SULFUR CYCLES AND ATMOSPHERIC OXYGEN: APPLICATION TO PALEOZOIC GEOLOGIC HISTORY

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ABSTRACT. A modification of the Garrels and Lerman (1984) isotope mass balance model has been constructed that uses new isotopic data and divides each reservoir of oxidized and reduced carbon and sulfur into young (rapidly-recycled) and old sub-reservoirs. This "rapid-recycling" model is used to see if conclusions based on the Garrels and Lerman model can be modified by maximizing the recycling of isotope signals between the oceans and various rock reservoirs. Results indicate that the very high burial rates of organic carbon calculated for Permo-Carboniferous time cannot be appreciably changed by rapid recycling but that the very high calculated burial ratio of organic-carbon-to-pyrite-sulfur at that time can be lowered. Using a simple oxygen calculation sub-routine, one can also show that oxygen levels were probably higher, than at present, during the mid-to-late Paleozoic, and this conclusion is independent of which model is used. This excess O_2, as well as elevated organic burial rates and higher mean C/S ratios for sediments, probably was caused by enhanced deposition and preservation of vascular land plant debris at that time.

INTRODUCTION

Background.—Several isotope mass balance models (for example Holser and Kaplan, 1966; Rees, 1970; Holland, 1973; Claypool and others, 1980; Schidlowski and Junge, 1981; Garrels and Lerman, 1984; Berner and Raiswell, 1983; Holland, 1984; Francois and Gerard, 1986; Kump and Garrels, 1986) have been constructed for calculating cycling rates of oxidized and reduced forms of carbon and sulfur at the Earth's surface over geologic time. This is important because the C-S sedimentary redox cycle exerts a major influence on the oxygen level of the atmosphere and the levels of dissolved carbon and sulfur in the ocean. The model of Garrels and Lerman (1984) is especially noteworthy in this respect. In this model values of $\delta^{13}C$ and $\delta^{34}S$ of ancient oceans, as recorded in limestones and evaporites respectively, are used to calculate worldwide rates of burial and weathering of (1) organic matter, (2) sedimentary carbonate rocks (limestone plus dolostone), (3) sedimentary pyrite, and (4) evaporitic $CaSO_4$ (gypsum plus anhydrite).

The Garrels and Lerman (1984) model is represented diagramatically in figure 1. Here the symbols C and S refer to masses of carbon and sulfur, F to fluxes between reservoirs, δ to isotopic composition, and the subscripts 1, 2, 3, 4, 5, and 6 to pyrite sulfur, $CaSO_4$ sulfur, oceanic sulfur, oceanic carbon, organic carbon, and carbonate rock carbon, respectively. Fluxes are denoted by subscripts given in the order of transfer; for example, the weathering flux of pyrite sulfur (1) to oceanic sulfur (3) is denoted as F_{13}.

In the Garrels and Lerman model, fluxes involving organic matter and pyrite constitute oxidation-reduction reactions, because carbon and sulfur are present in reduced forms in these substances whereas they occur in oxidized forms in the oceans and atmosphere. Such changes in oxidation state involve the uptake and release of atmospheric oxygen. Some representative reactions are:

Weathering (uptake of O_2):

$$\downarrow O_2 + CH_2O \rightarrow CO_2 + H_2O \qquad \text{(i)}$$

$$\downarrow 15O_2 + 4FeS_2 + 16CaCO_3 + 8H_2O \rightarrow 2Fe_2O_3 + 16Ca^{++} + 16HCO_3^- + 8SO_4^{--} \qquad \text{(ii)}$$

Sediment burial (release of O_2):

$$CO_2 + H_2O \rightarrow CH_2O + O_2\uparrow \qquad \text{(iii)}$$

$$2Fe_2O_3 + 16Ca^{++} + 16HCO_3^- + 8SO_4^{--} \rightarrow 4FeS_2 + 16CaCO_3 + 8H_2O + 15O_2\uparrow \qquad \text{(iv)}$$

Reactions (iii) and (iv), which are the reverse of reactions (i) and (ii), result from photosynthetic oxygen production. Burial of organic matter via reaction (iii) represents net photosynthesis over respiration, and, for

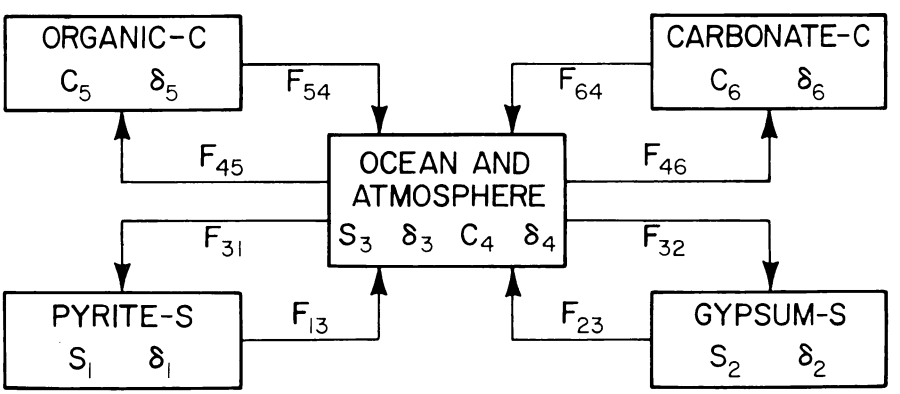

Fig. 1. Diagrammatic representation of the isotope mass balance model of Garrels and Lerman (1984). Symbols C and S refer to masses of carbon and sulfur, F to fluxes between reservoirs, and δ to isotopic composition in terms of standard delta notation. Subscripts 1, 2, 3, 4, 5, 6 refer, respectively, to pyrite-S, $CaSO_4$-S ("gypsum"), oceanic-S, oceanic-C, organic-C, $CaCO_3$-C. Flux subscripts refer to order of transfer (see text).

every mole of organic carbon buried, a mole of O_2 is left behind in the atmosphere. The O_2 produced in reaction (iv) comes about because organic matter produced via reaction (iii) is oxidized during bacterial sulfate reduction, not by O_2, but by oxygen in sulfate, leaving the original O_2 behind. From reactions (i) to (iv) it, thus, can be seen that the geochemical cycles of carbon and sulfur exert a major influence on levels of atmospheric oxygen. In fact, because of the relatively greater number of electrons transferred in these reactions, they overshadow oxidation-reduction reactions involving the other major redox sensitive element at the Earth's surface, iron.

Garrels and Lerman (see also Garrels and Perry, 1976; Holland, 1973; Schidlowski and Junge, 1981) have pointed out that, to avoid unacceptable excursions of atmospheric oxygen which would be lethal to higher organisms, large imbalances in the carbon system must be countered by corresponding changes in the sulfur system. In other words, one can combine the reactions given above, so as to eliminate O_2, to read (Garrels and Perry, 1974):

$$4FeS_2 + CaCO_3 + 7CaMg(CO_3)_2 + 7SiO_2 + 15H_2O \rightleftarrows \quad \text{(v)}$$
$$15CH_2O + 8CaSO_4 + 2Fe_2O_3 + 7MgSiO_3$$

Thus, reduction of carbon is stoichiometrically counterbalanced by oxidation of sulfur and vice versa. Put in another way, if over time there is more burial than weathering of organic carbon, resulting in transfer of carbon from the carbonate to the organic reservoir, then there must be a corresponding transfer from the pyrite to the $CaSO_4$ reservoir, resulting in a net accumulation of gypsum. One can show, also (see Kump and Garrels, 1986), that if there is an exact balance between the carbon and sulfur systems so as to prevent any variation in atmospheric oxygen, then the values of $\delta^{13}C$ and $\delta^{34}S$ for the ocean should bear a crude overall inverse linear relation to each other, and they, in fact, show this.

The picture summarized above, however, is too simple. Kump and Garrels (1986) have pointed out that sulfur and carbon isotopes have different response times to perturbations in the C-S cycle, because there is so much more seawater sulfate, in proportion to total sulfur at the Earth's surface, than there is seawater carbonate (see table 3). In addition, slight imbalances in the system due to other factors may actually have occurred in the geologic past bringing about moderate excursions in atmospheric oxygen (Holland, 1973, 1984; Walker, 1974). For example, Kump and Garrels (1986) and Shackleton (1985) suggest elevated O_2 levels relative to today during most of the past 100 my. Together, these considerations help explain why plots of $\delta^{13}C$ versus $\delta^{34}S$ show consistent deviations from a strictly linear relation. (Even at constant atmospheric O_2 such deviations would be expected due to the different response times — see Kump and Garrels, 1986. Also, the deviations cannot be explained only in terms of inaccuracy of measurement.) Thus, carbon-sulfur isotope mass balance modeling may be used to deduce changes in atmospheric oxygen levels

over geologic time (see Holland, 1973; Schidlowski and Junge, 1981). This was done by Kump and Garrels (1986) and Shackleton (1985) for the Cenozoic, and it is done for the whole Phanerozoic in the present paper.

The Garrels and Lerman model can be put to uses other than estimating atmospheric oxygen levels. Another application is calculation of the worldwide burial ratio of organic carbon to pyrite sulfur (C/S) in sedimentary rocks over Phanerozoic time (Berner and Raiswell, 1983; Berner, 1984). By means of the Garrels and Lerman model we have shown that fluctuations in the average C/S ratio can be explained in terms of shifts over time in the relative importance of organic matter burial in euxinic environments (low C/S), freshwater environments (high C/S), and normal marine environments (intermediate C/S).

TABLE 1

Expressions used in the Garrels and Lerman (simple) box model (refer to fig. 1). Definitions of symbols: C, S = masses of carbon and sulfur respectively in each reservoir (in 10^{18} moles); F = flux (in 10^{18} moles per my); k = first order weathering rate constant; δ = isotopic ratios of $^{34}S/^{32}S$ and $^{13}C/^{12}C$ expressed in standard δ notation; α_s, α_c = isotopic fractionation factors, for sulfur and carbon respectively, during deposition. (For further details consult Garrels and Lerman, 1984, and Kump and Garrels, 1986.)

Oceanic mass balance (assuming constant masses over time of C and S in ocean-atmosphere system)

$$F_{13} + F_{23} = F_{31} + F_{32}$$
$$F_{54} + F_{64} = F_{45} + F_{46}$$

Oceanic isotope mass balance (assuming succession of isotopic steady states in ocean each 1 million years)

$$\delta_1 F_{13} + \delta_2 F_{23} = (\delta_3 - \alpha_s) F_{31} + \delta_3 F_{32}$$

$$\delta_5 F_{54} + \delta_6 F_{64} = (\delta_4 - \alpha_c) F_{45} + \delta_4 F_{46}$$

Mass balance for each rock reservoir

$$dS_1/dt = F_{31} - F_{13}$$
$$dS_2/dt = F_{32} - F_{23}$$
$$dC_5/dt = F_{45} - F_{54}$$
$$dC_6/dt = F_{46} - F_{64}$$

Isotopic mass balance for each rock reservoir

$$d(\delta_1 S_1)/dt = (\delta_3 - \alpha_s) F_{31} - \delta_1 F_{13}$$
$$d(\delta_2 S_2)/dt = \delta_3 F_{32} - \delta_2 F_{23}$$
$$d(\delta_5 C_5)/dt = (\delta_4 - \alpha_c) F_{45} - \delta_5 F_{54}$$
$$d(\delta_6 C_6)/dt = \delta_4 F_{46} - \delta_6 F_{64}$$

Weathering fluxes

$$F_{13} = k_{13} S_1$$
$$F_{23} = k_{23} S_2$$
$$F_{54} = k_{54} C_5$$
$$F_{64} = k_{64} C_6$$

Rationale for present research.—Recently new $\delta^{13}C$ data for Permo-Carboniferous oceans have been obtained by Popp, Anderson, and Sandberg (1986). The data appear to be reliable, being based on unrecrystallized skeletal material, and they are independently confirmed by studies of reef cements by Given and Lohmann (1985) and Meyers and Lohmann (1985) and of brachiopods by Veizer, Fritz, and Jones (1986). The problem with the new data is that, when used in a Garrels and Lerman model calculation (see below), they bring about very high rates of organic carbon burial during the Permo-Carboniferous with correspondingly high levels of atmospheric oxygen and very high worldwide mean C/S ratio. The question then becomes could the Permo-Carboniferous world have had an appreciably higher O_2 level than today and could most organic matter burial have occurred on land, in freshwater swamps and lakes, as necessitated by the calculations. The purpose of the present paper is to pose and challenge these assertions.

One weakness of the Garrels and Lerman model is that organic matter, pyrite, carbonate, and $CaSO_4$ are lumped into a single reservoir box for each substance. This has the effect of providing a strong buffer against appreciable changes in the isotopic composition of weathering inputs to the ocean-atmosphere system. In fact, in the carbon system the mean isotopic value of the input of total carbon (organic plus carbonate) in the Garrels and Lerman model remains essentially constant over time. In this case the burial rate of organic carbon can be greatly simplified, from the expressions in table 1, to:

$$F_{45} = \frac{kC_t}{\alpha_c}(\delta_4 - \bar{\delta}) \qquad (1)$$

where:

F_{45} = burial rate of organic carbon

k = first order rate constant for weathering, assumed to be the same for carbonates and organic matter

C_t = total carbon in carbonate rocks plus organic matter, which is constant over time

α_c = fractionation factor for carbon isotope fractionation

δ_4 = oceanic $\delta^{13}C$ value

$\bar{\delta}$ = mean value of $\delta^{13}C$ for carbonates plus organic matter which is constant over time according to the model

Note that the only free variable on the right hand side of eq (1) is δ_4. (Values of α_c may fluctuate over time — Arthur, Dean, and Claypool, 1985 — but by no more than about ± 20 percent.) This means that the burial rate of organic matter, the major factor affecting atmospheric oxygen, is affected only by changes in δ_4, the $\delta^{13}C$ value for the ocean. Thus, one can see how large increases in δ_4, as found by Popp, Anderson, and Sandberg (1986), can result in large increases in organic carbon burial rate, F_{45}, and, consequently, in large inputs of O_2 to the atmosphere via reaction (iii).

The question, thus, arises whether it is possible to modify the Garrels and Lerman model so as to reduce fluctuations in burial rates, especially that of organic matter during the Permo-Carboniferous. This option is explored in the present paper. A double-box model is constructed that allows for rapid recycling of recently deposited carbon and sulfur. This is accomplished by dividing each rock reservoir into young and old components with weathering of the young component being employed to achieve rapid recycling. Conversion of young to old boxes, with a consequent reduction in weatherability, is done to mimic the natural process of deep sediment burial. In this way the isotopic value of inputs to the ocean can rapidly trace outputs and, thus, bring about a reduction in the fluctuation of calculated burial rates. (For example, in eq 1, allowing $\bar{\delta}$ to track δ_4 instead of remaining constant reduces variations in F_{45}.) This rapid recycling model was found to reduce pyrite burial rate fluctuations appreciably but *not* those for organic carbon. (Explanation of this is given later under *Results*.) Thus, the conclusion that O_2 levels were probably higher during the Permo-Carboniferous (Holland, 1984) could not be altered. On the other hand, it was possible to reduce mean C/S values for the Permo-Carboniferous, thus allowing for greater burial of organic matter under marine conditions than is permitted by use of the Garrels and Lerman model.

THEORY

Rapid-recycling model.—An isotope mass balance model was constructed by modifying the Garrels and Lerman (1984) model to include: (1) division of each carbon and sulfur reservoir into 2 sub-reservoirs representing young (rapidly recycled) and old rocks, and (2) use of independent carbon and sulfur isotopic data without any assumptions regarding coupling between the two (as was done in the original Garrels and Lerman model). A diagrammatic representation of the resulting *rapid recycling model* used here is shown in figure 2. As in the Garrels and Lerman model (fig. 1) symbols within boxes represent masses and isotopic values, and symbols along arrows represent fluxes from one reservoir to another. Nomenclature is analogous to that used by Garrels and Lerman (1984) except for the use of the subscripts Y and A for young and old ("ancient") reservoirs, respectively.

Since the reader may wish greater familiarization with the Garrels and Lerman model, a detailed summary of it is given in table 1. The mathematics of the modified or rapid-recycling model of the present paper is summarized in table 2. Notable features of the rapid-recycling model, in comparison with the simpler Garrels and Lerman model, are that weathering fluxes from rocks to the ocean-atmosphere arise from eight, rather than four, reservoirs, and young-to-old transfer rates (due to sediment burial) are assumed to be equal to weathering rates for the old rock reservoirs. In this way the old reservoirs are assumed to maintain constant mass. Note also that ocean-to-sediment burial fluxes pertain only to the young reservoirs, as is necessitated geologically.

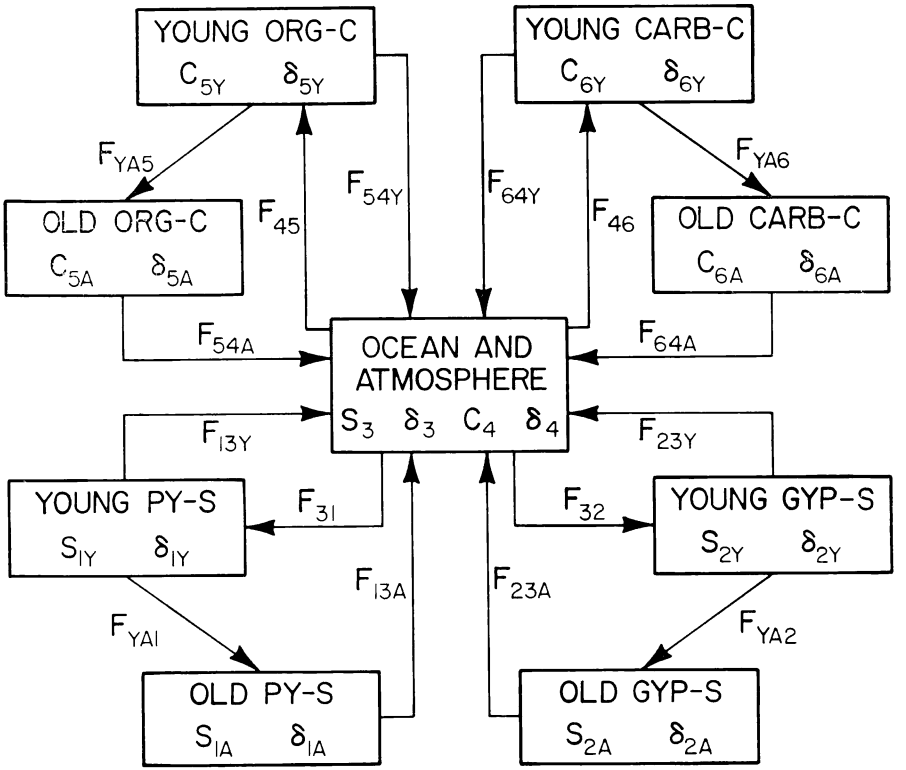

Fig. 2. Diagrammatic representation of the rapid-recycling isotope mass balance model of the present study. Subscripts Y and A refer to young and old (ancient) reservoirs respectively. Other symbols as in figure 1.

Oxygen calculation.—In order to calculate oxygen levels of the atmosphere a few amendations were made to the simple and rapid-recycling models. It was found (see Kump and Garrels, 1986) that some feedback of oxygen via weathering was necessary to prevent geologically unreasonable excursions of atmospheric oxygen. This feedback was accomplished by amending the weathering relations for oxidizable substances (pyrite and organic matter) by multiplying them by the factor $(O_2(t)/O_2(0))$. For example for the simple model:

$$F_{13} = (O_2(t)/O_2(0))k_{13}S_1 \quad (2)$$

$$F_{54} = (O_2(t)/O_2(0))k_{54}C_5 \quad (3)$$

Analogous weathering flux expressions for the rapid-recycling model were obtained also by multiplying by the factor $(O_2(t)/O_2(0))$. Here $O_2(t)$ refers to the mass of oxygen in the atmosphere at any time t, and $O_2(0)$ is the present day mass. These amended weathering flux equations express the reasonable assumption that oxidation during weathering increases with increasing levels of atmospheric O_2. In this way a negative feedback

TABLE 2

Expressions used in the rapid recycling box model (refer to fig. 2). Definition of symbols: C, S = masses of carbon and sulfur respectively in each reservoir (in 10^{18} moles); F = flux (in 10^{18} moles per my); k = first order weathering rate constant; δ = isotopic ratios of $^{34}S/^{32}S$ and $^{13}C/^{12}C$ expressed in standard δ notation; α_s, α_c = isotopic fractionation factors, for sulfur and carbon respectively, during deposition; subscripts Y and A refer to young and old (ancient) rocks respectively. Subscript YA refers to conversion flux of young to old rocks.

Oceanic mass balance (assuming constant masses over time of C and S in ocean-atmosphere system)

$$F_{13Y} + F_{13A} + F_{23Y} + F_{23A} = F_{31} + F_{32}$$

$$F_{54Y} + F_{54A} + F_{64Y} + F_{64A} = F_{45} + F_{46}$$

Oceanic isotope mass balance (assuming succession of isotopic steady states in ocean each 1 million years)

$$\delta_{1Y}F_{13Y} + \delta_{1A}F_{13A} + \delta_{2Y}F_{23Y} + \delta_{2A}F_{23A} = (\delta_3 - \alpha_S)F_{31} + \delta_3 F_{32}$$

$$\delta_{5Y}F_{54Y} + \delta_{5A}F_{54A} + \delta_{6Y}F_{64Y} + \delta_{6A}F_{64A} = (\delta_4 - \alpha_C)F_{45} + \delta_4 F_{46}$$

Mass balance for each rock reservoir (assuming constant mass of old (ancient) reservoirs)

$$dS_{1Y}/dt = F_{31} - F_{13Y} - F_{YA1} \qquad dS_{1A}/dt = F_{YA1} - F_{13A} = 0$$

$$dS_{2Y}/dt = F_{32} - F_{23Y} - F_{YA2} \qquad dS_{2A}/dt = F_{YA2} - F_{23A} = 0$$

$$dC_{5Y}/dt = F_{45} - F_{54Y} - F_{YA5} \qquad dC_{5A}/dt = F_{YA5} - F_{54A} = 0$$

$$dC_{6Y}/dt = F_{46} - F_{64Y} - F_{YA6} \qquad dC_{6A}/dt = F_{YA6} - F_{64A} = 0$$

Isotopic mass balance for each rock reservoir

$$d(\delta_{1Y}S_{1Y})/dt = (\delta_3 - \alpha_S)F_{31} - \delta_{1Y}F_{13Y} - \delta_{1Y}F_{YA1}$$

$$d(\delta_{1A}S_{1A})/dt = \delta_{1Y}F_{YA1} - \delta_{1A}F_{13A}$$

$$d(\delta_{2Y}S_{2Y})/dt = \delta_3 F_{32} - \delta_{2Y}F_{23Y} - \delta_{2Y}F_{YA2}$$

$$d(\delta_{2A}S_{2A})/dt = \delta_{2Y}F_{YA2} - \delta_{2A}F_{23A}$$

$$d(\delta_{5Y}C_{5Y})/dt = (\delta_4 - \alpha_C)F_{45} - \delta_{5Y}F_{54Y} - \delta_{5Y}F_{YA5}$$

$$d(\delta_{5A}C_{5A})/dt = \delta_{5Y}F_{YA5} - \delta_{5A}F_{54A}$$

$$d(\delta_{6Y}C_{6Y})/dt = \delta_4 F_{46} - \delta_{6Y}F_{64Y} - \delta_{6Y}F_{YA6}$$

$$d(\delta_{6A}C_{6A})/dt = \delta_{6Y}F_{YA6} - \delta_{6A}F_{64A}$$

Weathering Fluxes

$$F_{13Y} = k_{13Y}S_{1Y} \qquad F_{13A} = k_{13A}S_{1A}$$
$$F_{23Y} = k_{23Y}S_{2Y} \qquad F_{23A} = k_{23A}S_{2A}$$
$$F_{54Y} = k_{54Y}C_{5Y} \qquad F_{54A} = k_{54A}C_{5A}$$
$$F_{64Y} = k_{64Y}C_{6Y} \qquad F_{64A} = k_{64A}C_{6A}$$

"brake" is put on excessive atmospheric O_2 fluctuations. Also, it expresses the idea that during the weathering of pyrite and organic matter, all dissolved oxygen in ground water is consumed as would be reasonable for black and gray shales where most pyrite and organic matter are found. (Weathering during erosion, in the presence of excess O_2, as envisaged by Walker, 1974, is less likely.)

The differential expressions for O_2 levels in the atmosphere based on the stoichiometry of reactions (i)-(iv) are, thereby:

For the simple (Garrels and Lerman) model:

$$d\,O_2(t)/dt = (F_{45} + (15/8)F_{31}) - (F_{54} + (15/8)F_{13}) \tag{4}$$

For the rapid-recycling model:

$$d\,O_2(t)/dt = (F_{45} + (15/8)F_{31}) - (F_{54y} + F_{54A} + (15/8)F_{13y} + (15/8)F_{13A}) \tag{5}$$

Using the oxygen-feedback-amended expressions for F_{13}, F_{13y}, F_{13A}, F_{54}, F_{54y}, and F_{54A}, changes in O_2 over time can be calculated. However, a rigorous solution in this manner was found to be impossible for all Phanerozoic time because of a new positive feedback of oxygen in the calculation of F_{45} and F_{31}, the burial rates of organic carbon and pyrite sulfur, respectively. This problem arises from the presence of the weathering fluxes in the expressions for F_{45} and F_{31} (see tables 1 and 2). In simpler terms consider the following scenario. (I am grateful to Antonio Lasaga and Lee Kump for this description.) Suppose the organic burial rate, F_{45}, decreases. This results in a lower flux of O_2 to the atmosphere and, consequently, to a lower atmospheric O_2 level. The lower O_2 level, in turn, manifests itself via the decreased weathering of organic carbon as shown by eq (3) above. This decreased weathering delivers less total carbon and less ^{12}C (relative to ^{13}C) to the ocean which results, in order to preserve a constant isotopic composition and level of carbon there, in decreased organic carbon burial. Thus, an initial decrease in carbon burial is amplified by further decreases and the perturbation grows. Proceeding forward in time it was found that fluctuations in organic carbon burial resulted in unacceptable fluctuations in oxygen level (including negative values) when using the rigorous method.

To avoid the problem of excessive fluctuation, two approximate methods were tried. The first, as derived by Antonio Lasaga (personal commun.) involves the use of unamended (that is, Garrels-Lerman original) expressions for each of the weathering fluxes in the expressions for F_{45} and F_{31} but amended values (for example, eqs 2 and 3) in all other expressions. This succeeded in eliminating most problems in the simple model but still produced physically unreasonable results in the rapid-recycling model. The second method involves use of unamended weathering fluxes in all expressions except those for O_2 (eqs 4 and 5) where amended equations of the form of (2) and (3) are used. This method resulted in physically reasonable results for both the simple and rapid

recycling models and is the approach used here. In effect, this method adds a simple sub-routine for calculating O_2 to the main program.

Neither approximate method is, strictly speaking, physically correct (amended weathering flux expressions should be used consistently throughout). Nevertheless, the whole reason for calculating O_2 levels here is simply to show the *relative* consequences of changing recycling models on burial of organic matter and pyrite and atmospheric O_2 levels. Since the linear O_2 feedback used in the amended weathering expressed is merely an assumption anyway, the approach used to calculate O_2 levels is deemed sufficient for the purposes of the present paper. However, in future work, a better method of calculating O_2 should be devised.

Calculation method.—It was found to be impossible to use the "movie" model of Garrels and Lerman (1984), whereby present values for the various fluxes and reservoir masses are used at t = 0, and then earlier values are calculated by moving backward through time. This was because, for the rapid-recycling model, the approach resulted in numerical blowup. This is an example of the well known observation that multi-feedback box models, which lead to stability going forward in time, result in instability going backward (for example, see Lasaga, 1980; Berner, Lasaga, and Garrels, 1983). The alternate method used was to assume present day conditions at 570 my BP and to move forward to the present. This approach (see also Garrels and Lerman, 1984) resulted in recovery of values at t = 0, for all parameters, reasonably close to those for the present day. This suggests that the "world" at the beginning of the Cambrian was rather similar to that at present. (See Garrels and Lerman, 1984, for further discussion of this intriguing idea.)

Values of rate constants, initial masses, and $\delta^{13}C$ and $\delta^{34}S$ values used in the calculations are given in table 3 and figure 3. The oceanic carbon

TABLE 3

Values of parameters used in the isotope mass-balance calculations. (For a definition of symbols see tables 1 and 2 and figs. 1 and 2.) Masses in 10^{18} moles; fluxes in 10^{18} moles/my; rate constants in my^{-1}. The values for S, C, and δ represent initial (starting) values for 570 my BP. $\alpha_s = 35‰$, $\alpha_c = 25‰$ for both models.

Simple Model	Rapid-recycling Model	
S_3 = 38	S_3 = 38	C_4 = 2
C_4 = 2	S_{1Y} = 30	S_{1A} = 220
S_1 = 250	S_{2Y} = 30	S_{2A} = 220
S_2 = 250	C_{5Y} = 150	C_{5A} = 1100
C_5 = 1250	C_{6Y} = 600	C_{6A} = 4400
C_6 = 5000	$k_{13Y} = 1.78\times10^{-2}$	$k_{13A} = 6.05\times10^{-4}$
$k_{13} = 2.67 \times 10^{-3}$	$k_{23Y} = 3.56\times10^{-2}$	$k_{23A} = 1.21\times10^{-3}$
$k_{23} = 5.34 \times 10^{-3}$	$k_{54Y} = 2.67\times10^{-2}$	$k_{54A} = 9.09\times10^{-4}$
$k_{54} = 4.00 \times 10^{-3}$	$k_{64Y} = 2.67\times10^{-2}$	$k_{64A} = 9.09\times10^{-4}$
$k_{64} = 4.00 \times 10^{-3}$	F_{YA1} = 0.133	F_{YA2} = 0.267
δ_1 =-15‰	F_{YA5} = 1	F_{YA6} = 4
δ_2 = 20‰	δ_{1Y} =-17.0‰	δ_{1A} =-15.0‰
δ_5 =-23.5‰	δ_{2Y} = 18.0‰	δ_{2A} = 20.0‰
δ_6 = 1.5‰	δ_{5Y} =-23.5‰	δ_{5A} =-23.5‰
	δ_{6Y} = 1.5‰	δ_{6A} = 1.5‰

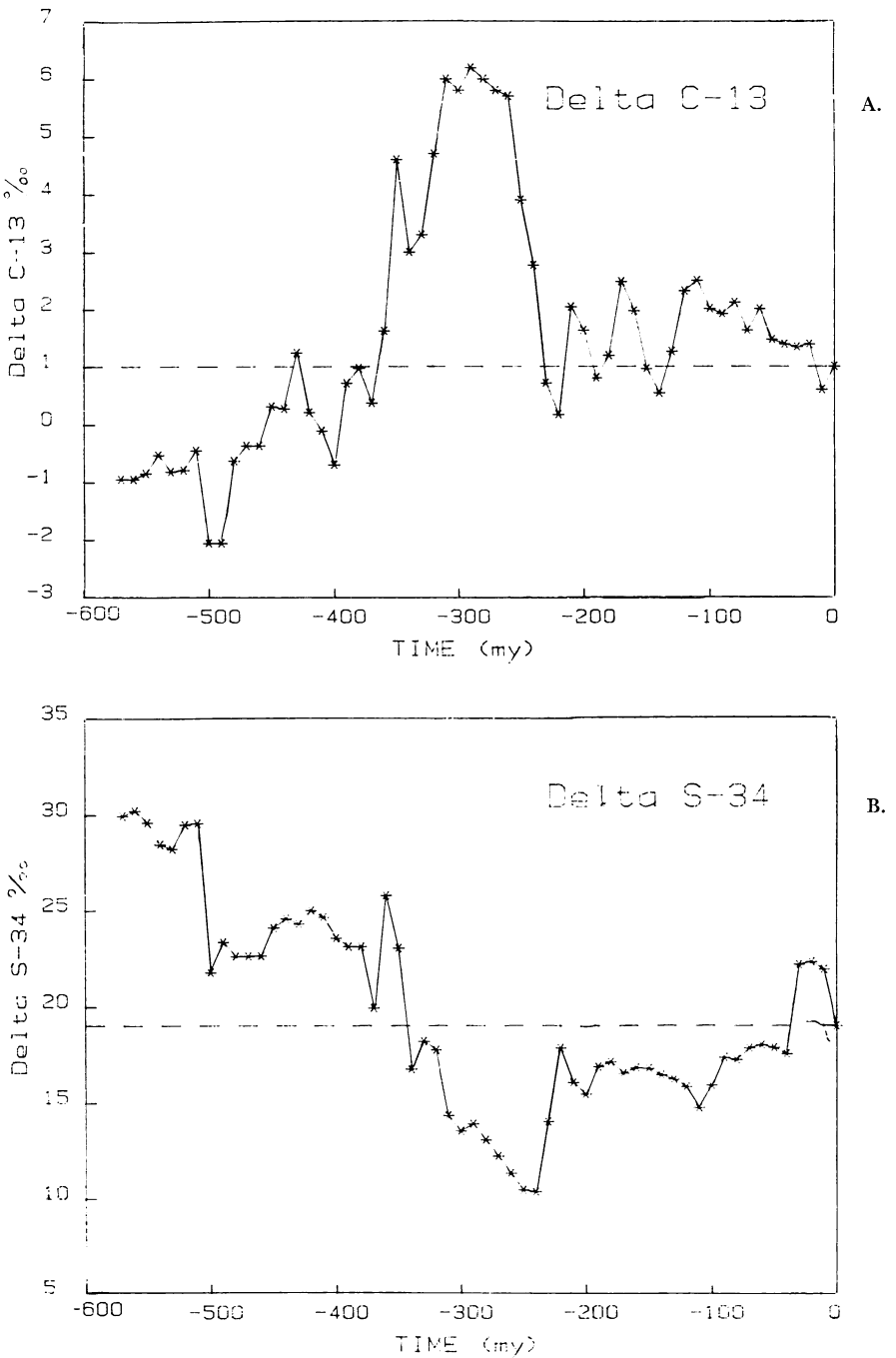

Fig. 3. Carbon and sulfur isotopic data (in terms of $\delta^{13}C$ and $\delta^{34}S$) for seawater as a function of geologic time based on the data compilation of Lindh (ms) updated to include the Permo-Caroniferous $\delta^{13}C$ values of Popp, Anderson, and Sandberg (1986). (A) carbon; (B) sulfur.

and sulfur isotopic data are taken from Lindh (ms) modified to include recent values for $\delta^{13}C$ for Permo-Carboniferous oceans reported by Popp, Anderson, and Sandberg (1986). Values used in the rapid-recycling model calculation represent an arbitrarily chosen extreme situation set-up so as to maximize recycling of recently deposited carbon and sulfur. Constraints in selecting values for the rapid-recycling model were that initial values for *total* (old plus young) reservoir sizes and total weathering inputs to the ocean-atmosphere be the same as those used in the simple model calculations, and that young-old transfer fluxes be equal to weathering rates for each of the old reservoirs, so as to maintain constant old-reservoir size.

The numerical method used in the calculations is simple. It is assumed that at each successive million year point, starting at 570 my BP, a separate ocean-plus-atmosphere steady state is attained. Thus, the changing $\delta^{13}C$ and $\delta^{34}S$ values are used to calculate new steady-state values for fluxes, masses, and rock isotopic composition, at the end of each one-millon year period. This method is essentially valid when compared with results of more complicated numerical techniques, and it helps to smooth out results from sudden variations in the isotopic data.

RESULTS

Results are expressed, in terms of plots versus time, for organic carbon burial (F_{45}) in figure 4, for mean C/S ratio in figure 5, and for oxygen level in figure 6. In each figure results for the simple, or Garrels and Lerman, model are compared with those for the rapid-recycling model. In order to maximize recycling rates in the latter model, extreme values were chosen for relative sizes and weathering rates. (Young reservoirs were assumed to be one-seventh as large as old reservoirs and to have initial weathering fluxes four times larger than those for the old reservoirs.) This division of rock carbon and sulfur into very different young and old reservoirs was done simply to illustrate the effects of very rapid recycling of isotopes to-and-from the ocean, and the values chosen here are geologically unreasonable. (For example, the resulting young-to-old transfer rates give young-reservoir life-times that are too long when compared to the mass-age distribution for sedimentary rocks — see Gregor, 1983.)

Comparison of results for the two models shows that use of a rapid recycling model does not result in appreciable reduction of the large peak of high Permo-Carboniferous organic carbon burial rates at 350 to 250 my (fig. 4). Why should there be little or no effect of increased recycling rates on organic burial rates? As we have already stated, consideration of eq (1) suggests that there should be an effect, but, yet, there isn't.

The explanation for the lack of sensitivity of organic carbon burial and oxygen production to recycling rates lies in the nature of the carbon isotope data and its relation to the model calculations. An equation for

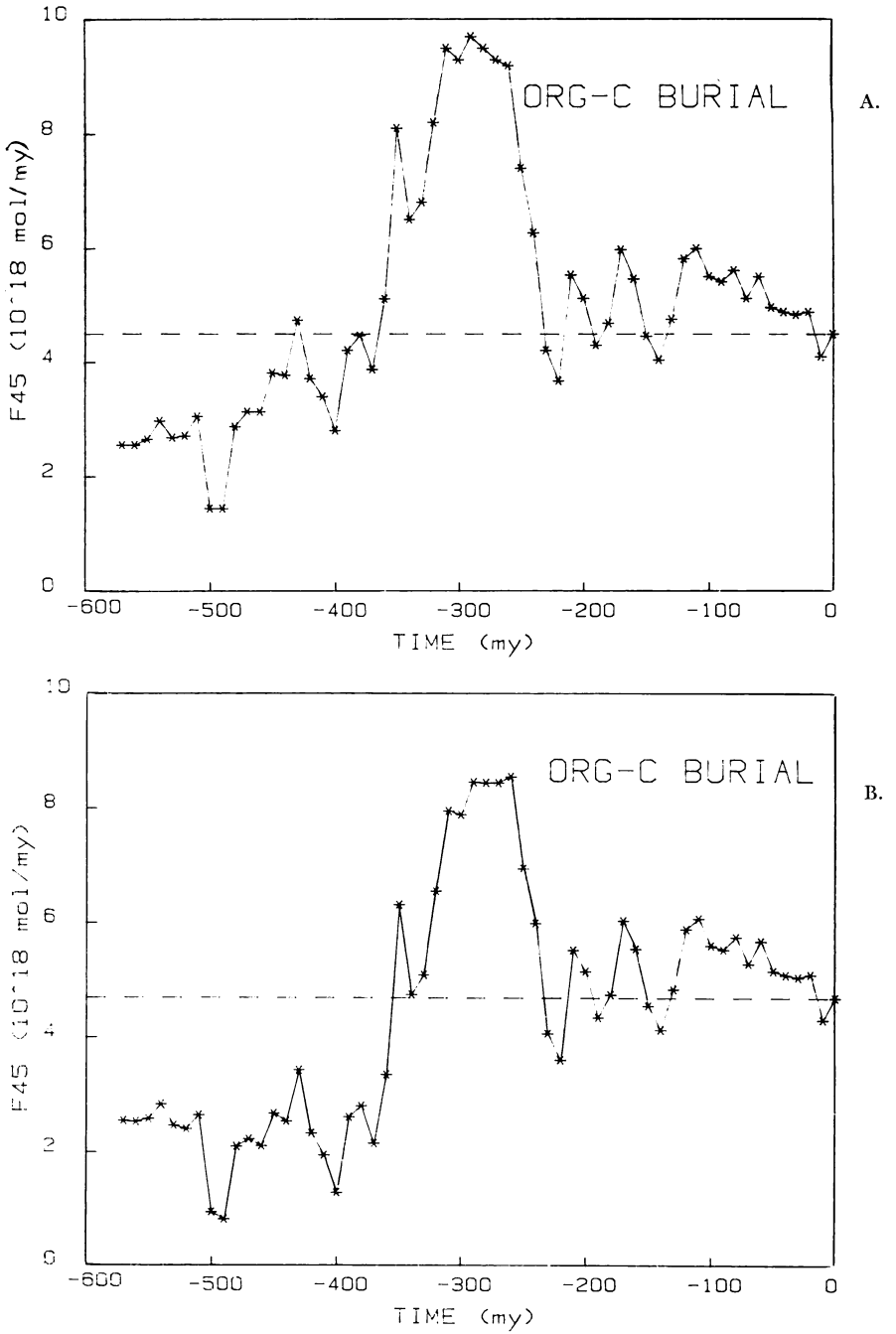

Fig. 4. Comparison of results for the worldwide burial rate of organic carbon (F_{45} in 10^{18} moles per my) vs time calculated via the simple Garrels and Lerman model and the rapid-recycling model of the present study. Data used for calculations shown in table 3. (A) model of Garrels and Lerman (1984); (B) present rapid-recycling model.

the recycling model, analogous to that for eq (1) (which can be derived directly from the expressions in table 2) is:

$$F_{45} = (1/\alpha_c)[k_y C_{T_y} (\delta_4 - \bar{\delta}_y) + k_A C_{T_A} (\delta_4 - \bar{\delta}_A)] \quad (6)$$

where:

F_{45} = organic carbon burial rate
α_c = fractionation factor for organic carbon
C_{T_y}; C_{T_A} = total concentration of carbon (organic plus carbonate) in the young and old reservoirs, respectively, (both constant)
k_y; k_A = weathering rate constants for the young and old reservoirs, respectively (note that $k_{5y} = k_{6y}$ and $k_{5A} = k_{6A}$ in table 3 so that $k_y \equiv k_{5y} = k_{6y}$ and $k_A \equiv k_{5A} = k_{6A}$)
δ_4 = oceanic $\delta^{13}C$ value
$\bar{\delta}_y$ = $(C_{5y}\delta_{5y} + C_{6y}\delta_{6y})/C_{Ty}$ = mean δ value for the young carbon reservoirs
$\bar{\delta}_A$ = $(C_{5A}\delta_{5A} + C_{6A}\delta_{6A})/C_{TA}$ = mean δ value for the old carbon reservoirs

Now, during the runs it was found that $\bar{\delta}_A$ was essentially constant (because of the large size and slow recycling rate of the old reservoirs), and since k_y, k_A, C_{T_y}, C_{T_A}, and α_c are all defined as constant by the model, the only time-dependent variables, on the right-hand side of this expression, are δ_4 and $\bar{\delta}_y$. If there is rapid recycling, one would expect $\bar{\delta}_y$ to track δ_4. In other words, as the δ value of the ocean rises the small, young rapidly-recycling reservoirs should quickly sense this shift resulting in a corresponding rise in $\bar{\delta}_y$. This should prevent large excursions in F_{45} because the difference $(\delta_4\text{-}\bar{\delta}_y)$ would remain constant. $(\delta_4\text{-}\bar{\delta}_A$ would change, but its effect is small because of the very low value of k_A.) However, this reasoning fails to take into account changes in the relative *sizes* of the young organic and carbonate reservoirs (both of which are small and easily perturbed). During the Permo-Carboniferous, the sudden shift to very high isotopic values for the ocean (see fig. 3) brings about high rates of organic carbon burial. This results in the rapid growth of the young organic-carbon reservoir at the expense of the young carbonate-carbon reservoir. Since δ values are far lower for organic carbon, this shift in mass causes the mean value for the young reservoirs $\bar{\delta}_y$ to *decrease*. This occurs even though the ocean is feeding heavy carbon to both the young organic and carbonate reservoirs, and the $\bar{\delta}_y$ value should, thereby, *increase* in order to track δ_4. But it doesn't. Because the δ_4 values for the Permo-Carboniferous ocean are so high and the young reservoir sizes are so small, the transfer of carbon from the carbonate to the organic reservoir overpowers the addition of heavy carbon to both reservoirs from the ocean. Thus, $\bar{\delta}_y$ falls while δ_4 rises. This gives rise to large values of F_{45}, and the whole purpose of using a rapid-recycling model is defeated.

Use of more equal-sized young and old reservoirs helps to get rid of the carbonate-to-organic carbon mass transfer problem, but then the

larger sizes of the young reservoirs result in slower isotope recycling. It was found, by trial and error, that no matter how one adjusts the relative sizes and weathering rates of the young and old reservoirs, organic carbon burial rates during the Permo-Carboniferous remain high and similar to values calculated via the simple Garrels and Lerman model. Furthermore, use of an alternative (but geologically less tenable) formulation for the rapid recycling model, where the masses of each of the young reservoirs are held constant over time and increased burial of organic matter results simply in increased conversion of young organic matter to old (L. R. Kump, personal commun.), while better reducing time variations still results in excessive organic burial during the Permo-Carboniferous.

The situation for pyrite burial was found to be different. The very low burial rates for pyrite sulfur calculated via the Garrels and Lerman model for Upper Carboniferous-Permian time ($0.1\text{-}0.3 \times 10^{18}$ mol/my) are considerably increased using the rapid recycling model ($0.4\text{-}0.6 \times 10^{18}$ mol/my). This is due to the fact that, over Devonian-Carboniferous time, using the rapid recycling model there is a lower mean $\delta^{34}S$ value for the weathering input to the ocean-atmosphere, and this leads to higher calculated pyrite burial rates. (Further explanation of this in terms of an equation of the form of (6) is impossible, because such a relatively simple expression cannot be derived for the sulfur system due to the fact that the weathering constants, k, for pyrite and $CaSO_4$ are different.) Most importantly, the increase in pyrite sulfur burial rates, combined with no appreciable change in rates of organic carbon burial, results in lower mean C/S ratios for the Permo-Carboniferous, when calculated via the rapid-recycling model. This is shown in figure 5.

The net effect on O_2 levels of changing from the Garrels and Lerman model to the rapid-recycling model is shown in figure 6. As one can see there is a diminishment of the large Permo-Carboniferous peak but not its removal. The major reason for the lack of collapse of the O_2 peak is the small relative change in organic carbon burial rates between the two models (fig. 4). Thus, use of a rapid-recycling model cannot alter the conclusion that higher atmospheric oxygen levels occurred during Permo-Carboniferous time.

APPLICATION TO PALEOZOIC GEOLOGIC HISTORY

Use of either the simple or rapid-recycling isotope mass balance models (fig. 4) leads to the conclusion that worldwide organic matter burial rates have varied considerably over Phanerozoic time. Values lower than today are characteristic of the early Paleozoic, and values much higher than today of the later Paleozoic. What could have brought about this large increase in rates? I believe the primary cause was the rise of vascular plants on the continents during the Silurian and their subsequent major radiation. This new form of plant life led to a major new source of organic matter for deposition in sediments. Vascular land plant debris could be buried either on the continents, in swamps, lakes, bogs, et cetera, or in marine sediments upon transport to the oceans by rivers. Also, because

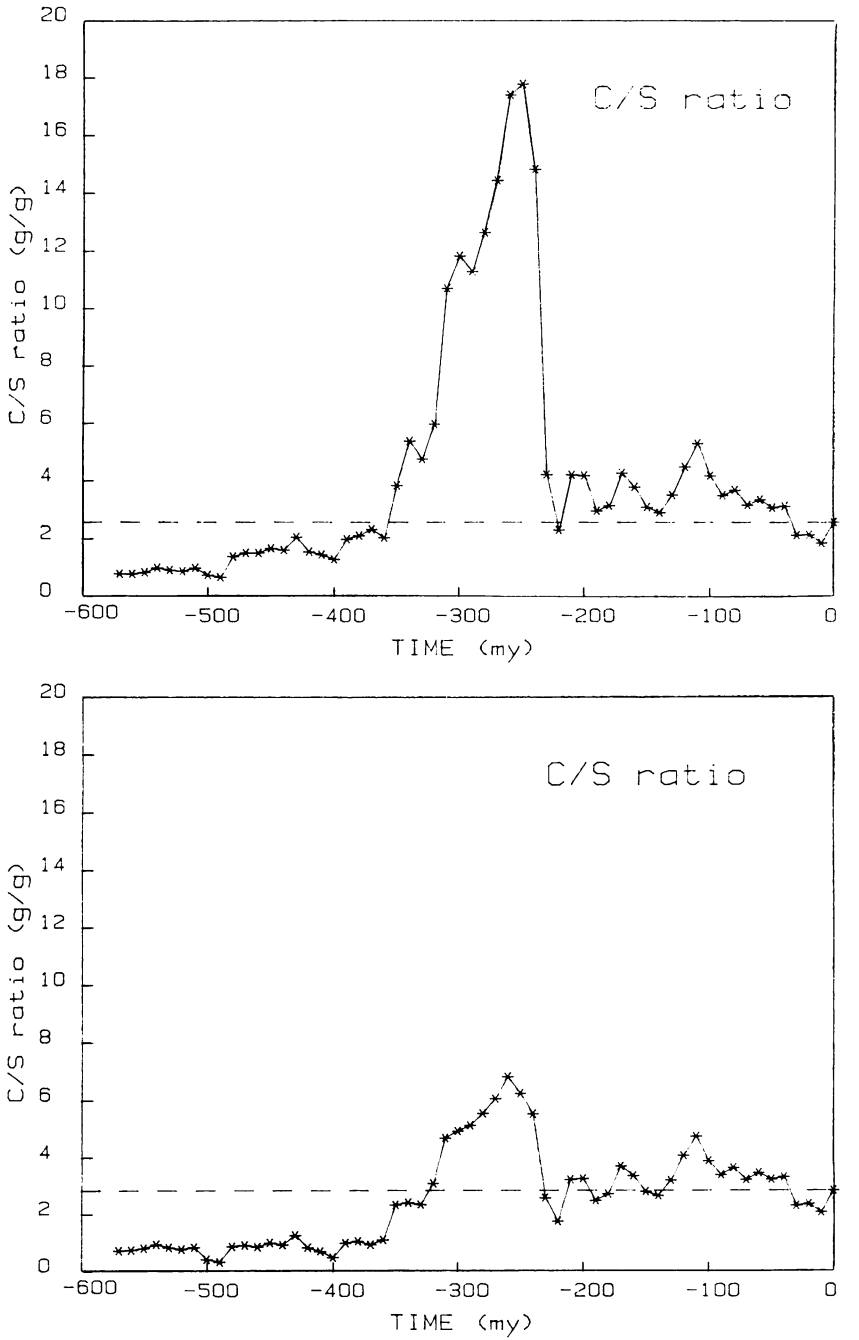

Fig. 5. Comparison of results for C/S, the ratio of worldwide burial rates of organic carbon and pyrite sulfur (F_{45}/F_{81} converted to grams per gram) versus time calculated via the simple Garrels and Lerman model and the rapid recycling model of the present study. Data used for calculations shown in table 3. (A) model of Garrels and Lerman (1984); (B) present rapid-recycling model.

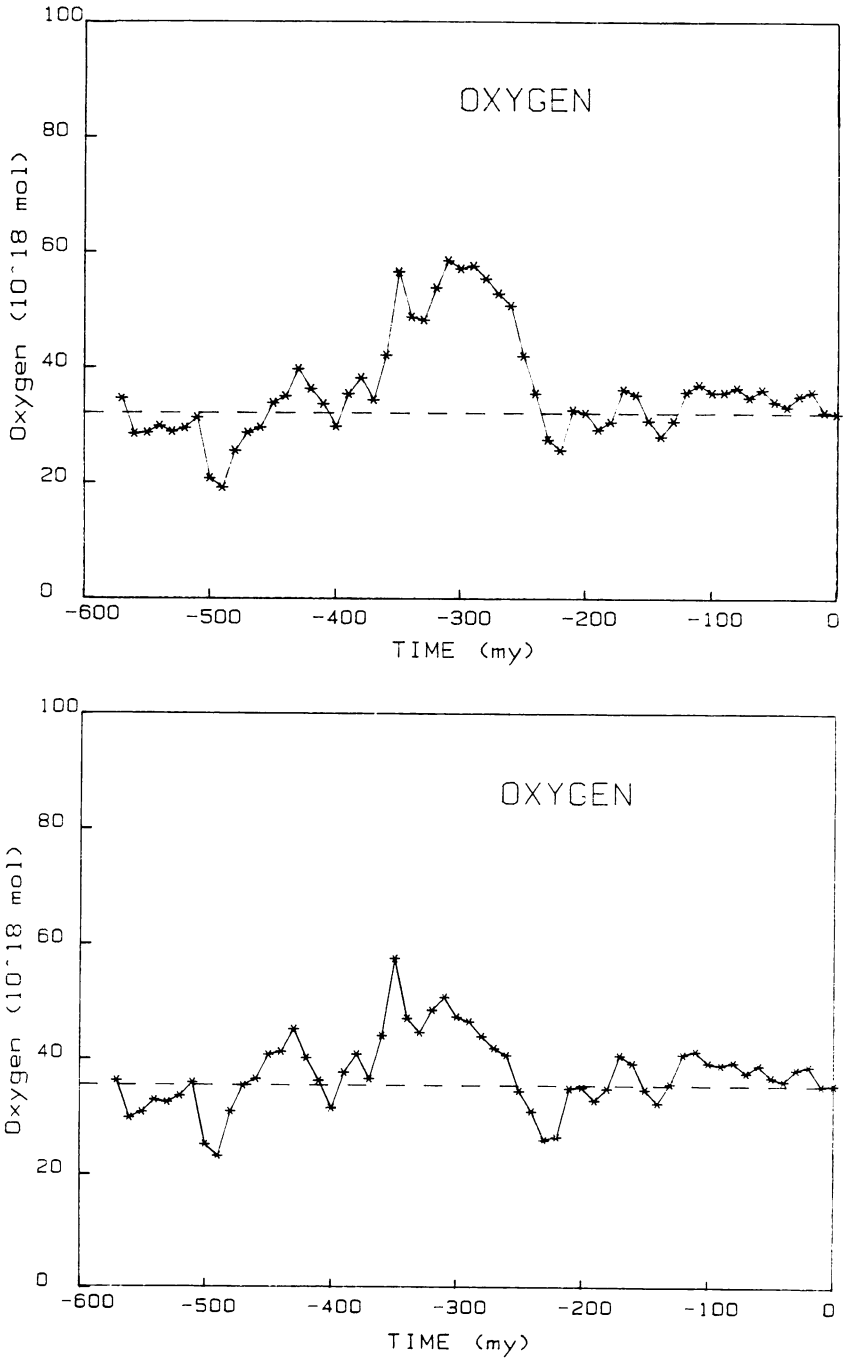

Fig. 6. Comparison of results for atmospheric oxygen (in 10^{18} moles) versus time calculated via the simple Garrels and Lerman model and the rapid recycling model of the present study. Data used for calculations shown in table 3. (A) model of Garrels and Lerman (1984); present rapid-recycling model.

of a high C/P ratio, more carbon could be buried per unit of nutrient phosphorus supplied. An additional cause of increased organic carbon burial was the availability of large areas of flooded lowlands on the emergent Permo-Carboniferous supercontinent of Pangea where organic matter, once deposited, could be preserved. Attestation to the efficacy of both vascular land plant production and extensive preservation of organic debris in swamps, lakes, et cetera, during the Permo-Carboniferous is given by the vast coal deposits laid down at that time. (It should be noted that preliminary data for the late Proterozoic — Magaritz, Holser, and Kirschvink, 1986; Tucker, 1986; Knoll and others, 1986 — also indicate high oceanic $\delta^{13}C$ values and correspondingly high organic carbon burial rates. Since during this period vascular land plants were absent, another process, such as increased marine production, must have brought about the excessive burial rates.)

Accompanying the large increase in organic carbon burial rates during the Paleozoic was a large increase in the calculated mean ratio of organic carbon to pyrite sulfur (C/S) in sediments. This is shown in figure 5. This increase has been explained (Berner and Raiswell, 1983; Berner, 1984) as being due to a shift in the location of major organic matter burial from marine to terrestrial environments. It is based on the observation that C/S ratios of modern non-marine organic-rich sediments are appreciably higher than those for marine sediments (Berner and Raiswell, 1984). If one accepts the rapid recycling results as being more nearly correct, then one can calculate the relative proportions of organic burial in marine and non-marine environments during the Permo-Carboniferous. The reasoning is as follows: Assume that during the Permo-Carboniferous organic matter was deposited in marine environments, with a S:C weight ratio of 1:3 like today (Berner, 1984) and in non-marine environments with a S:C weight ratio of about 1:20 also like today. (The exact value of the non-marine S:C ratio is not important to the calculation as long as it is much less than 1:3.) Then for mass balance, one can show that:

$$(S/C)_{PC} = (S/C)_{MAR}(1 - f_c) + (S/C)_{NM}\, f_c$$

where:

$(S/C)_{PC}$ = Permo-Carboniferous mean S/C ratio = 1/6
$(S/C)_{MAR}$ = present day marine S/C ratio = 1/3
$(S/C)_{NM}$ = present day non-marine S/C ratio = 1/20
f_c = fraction of total Permo-Carboniferous organic matter deposition that took place on the continents in fresh water

Solving for f_c, we obtain:

$$f_c = 0.59$$

The above calculation shows that a major portion (59 percent) of organic matter deposition during the Permo-Carboniferous period would have to have been deposited in fresh water to sustain a mean value of C/S = 6 for all Permo-Carboniferous sediments, as calculated by the rapid-recycling model. If the simple Garrels and Lerman model is used,

the number rises to greater than 90 percent. Although the latter value seems excessive, there is little doubt that if the calculations presented here are at all realistic, a large proportion of total world-wide organic matter burial during the Permo-Carboniferous period took place on land in fresh water. Independent calculations based on the measured abundance of non-marine organic matter, including coal, for this time period support this conclusion (Berner, 1984).

Finally, a major consequence of increased organic carbon burial during the mid-to-late Paleozoic was an increased input of O_2 to the atmosphere, which must have manifested itself in terms of increased atmospheric O_2 levels. The actual values shown in figure 6 are highly dependent upon a certain type of linear feedback model and are *not to be taken too literally*. Nevertheless, the rapid recycling model (which was used as a maximum effort to reduce time variations) was unsuccessful in bringing about elimination of the oxygen peak. Thus, it appears from what we know at present, that O_2 levels during mid-to-late Paleozoic time were higher than they are today, an idea already put forward by Holland (1984). If this is true, there must be some recognizable geological consequences, and the author feels that the best hope lies in examining the fossil record for organisms that might indicate elevated O_2 levels (an initial step in this direction has been taken by McAlester, 1970, and Paul, 1976). Another possible approach is to look for evidence of greater forest fire damage as predicted by Watson, Lovelock, and Margulis (1978) for higher atmospheric oxygen levels. Confirmation or refutation of the idea of fluctuations in atmospheric O_2 over Phanerozoic time awaits further geological inquiry!

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