

A NEW APPROACH TO ISOTOPIC MODELING OF THE VARIATION OF ATMOSPHERIC OXYGEN THROUGH THE PHANEROZOIC

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ABSTRACT. The use of stable isotopes as inputs to modeling the redox geochemical cycles is analyzed. A major correction to earlier models arises from the need to use the time derivatives of δ (obtained from the measured δ versus time data) directly in the calculations. This correction is much more important for the sulfur system than for the carbon system.

The rise of an "oxygen catastrophe" in earlier isotope models of the redox cycles leads to a new method of handling the dynamics of geochemical cycles that is based on minimization of a statistical function. The statistical function not only incorporates the usual mass balance expressions but also includes constraints on geochemical fluxes. This statistical model not only solves the "oxygen catastrophe" but also can be generalized to many other future applications.

INTRODUCTION

Nature is undoubtedly complex; nonetheless, earth scientists try to unravel at least some of the processes that have been operative during Earth's history. To accomplish this feat, we must utilize the meager data available and the chemical constraints imposed by general observations of both biota and the inorganic realm. Immediately a problem arises from the enormous number of "variables" that should be included in a comprehensive model of elemental transfer within the Earth. Typically, we first compartmentalize the workings of nature into "boxes," that is, the so-called box models, and then drastically reduce the number of boxes to a manageable size, usually countable with one's fingers.

The models born of this approach suffer from several ailments. Clearly, the fluxes between all the boxes occur in a multitude of ways, and the dynamical description of a total flux becomes intertwined with an averaging over many processes. Extracting a dynamical equation from this averaging can be quite demanding! On the other hand, boxes not included in the model can have a "hidden variable" effect on the simple system. The result can be anything from a stochastic random fluctuation to a well-defined periodic perturbation on the system. As a consequence, the dynamical operation of the system is often in conflict with several chemical or physical constraints. This problem can be ameliorated by the initiation of box models that include a statistical treatment of general geochemical constraints as will be elaborated in this paper.

SIMPLE MODEL

We will begin with a description of the simple model. The biggest controls over the oxygen in the atmosphere on geologic time scales are

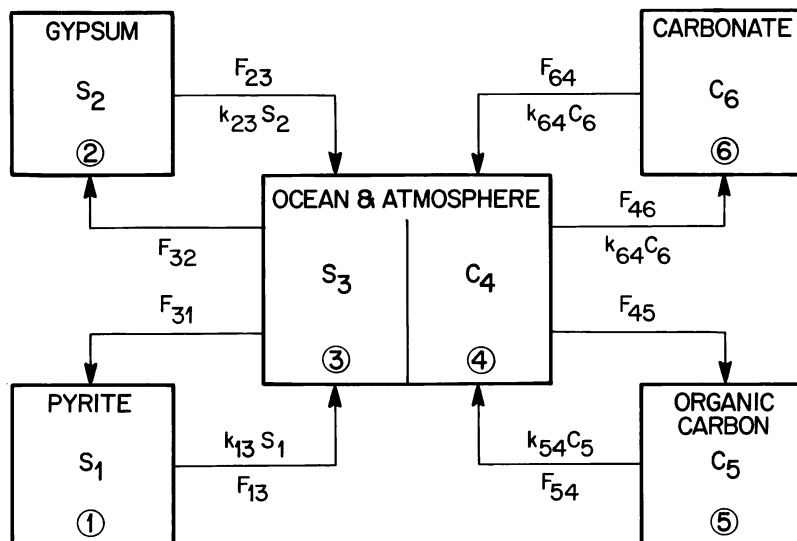


Fig. 1. Box model for the carbon-sulfur isotope system.

the changes in the redox cycles of carbon and sulfur and to a lesser extent iron. As a result, these essential processes are incorporated into the geochemical cycle as illustrated in the by-now-traditional box model given in figure 1. In terms of dynamics, one of the hardest terms to predict from ab-initio principles is the *net* burial rate of organic carbon and reduced sulfur in marine sediments. Undoubtedly, these fluxes will depend on nutrient input, photosynthetic activity, dissolved oxygen profile in the oceans, sedimentation rate, temperature, and so on. One way that these fluxes have been incorporated into geochemical models is by use of the measured variations in sulfur and carbon isotope variations (Holland, 1973; Garrels and Lerman, 1981, 1984; Lasaga, Berner, and Garrels, 1984; Berner and Raiswell, 1983; Kump and Garrels, 1986; Berner, 1987). The basic idea behind the use of isotopes is that the instantaneous value of $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ in the oceans at a given time is a function of the relative balance between inputs and outputs as represented by the fluxes shown in figure 1.

The simplest (and most common!) way to proceed is to set up oceanic mass balance for both C and S as well as their isotopes (refer to fig. 1):

$$F_{13} + F_{23} = F_{31} + F_{32} \quad (1)$$

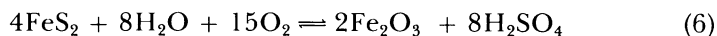
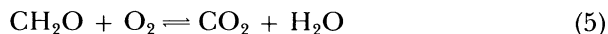
$$F_{54} + F_{64} = F_{45} + F_{46} \quad (2)$$

$$\delta_1 F_{13} + \delta_2 F_{23} = (\delta_3 - \alpha_s) F_{31} + \delta_3 F_{32} \quad (3)$$

$$\delta_5 F_{54} + \delta_6 F_{64} = (\delta_4 - \alpha_c) F_{45} + \delta_4 F_{46} \quad (4)$$

Note that eqs (1) to (4) presume that there is no change in the total amount of HCO_3^- or SO_4^{2-} in the oceans as well as no change in $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$: that is, complete oceanic steady state! Obviously, this is a crude approximation and, in particular, eqs (3) and (4) are not strictly consistent with the use of a varying $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ in the model. To what extent (3) and (4) are permissible (as used by Garrels and Lerman, 1984; Lasaga, Berner, and Garrels, 1984; Kump and Garrels, 1986; Berner, 1987; and Berner and Raiswell, 1983) will be discussed later in the paper. Eqs (3) and (4) assume no fractionation during weathering or in the deposition of carbonates. They also assume a constant fractionation factor of α_s or α_c during the deposition of reduced sulfur and reduced organic matter respectively.

Whatever the values of the fluxes in eqs (1) to (4), the rate of change of oxygen in the atmosphere can be obtained from the reactions:



Combining reactions (5) and (6), we obtain:

$$\frac{dS_{\text{O}_2}}{dt} = F_{45} + \frac{15}{8} F_{31} - \frac{15}{8} F_{13} - F_{54} \quad (7)$$

where S_{O_2} is the mass of oxygen in the atmosphere.

Eqs (1) to (4) and (7) have 8 unknown fluxes. The weathering fluxes are usually specified by assuming a first-order kinetic model:

$$F_{13} = k_{13} S_1 \quad (8)$$

$$F_{23} = k_{23} S_2 \quad (9)$$

$$F_{54} = k_{54} C_5 \quad (10)$$

$$F_{64} = k_{64} C_6 \quad (11)$$

If we were to specify the 4 weathering fluxes, eqs (1) to (4) would enable solution of the remaining 4 depositional fluxes, as long as α_s and α_c and $\delta^{13}\text{C}$, $\delta^{34}\text{S}$ values for the reservoirs are known through time. To obtain δ_1 , δ_2 , δ_5 , δ_6 as a function of time, we must use the equations:

$$\frac{d(\delta_1 S_1)}{dt} = S_1 \frac{d\delta_1}{dt} + \delta_1 \frac{dS_1}{dt} = (\delta_3 - \alpha_s) F_{31} - \delta_1 F_{13}$$

Inserting the relation:

$$\frac{dS_1}{dt} = F_{31} - F_{13}$$

into the above we obtain,

$$\frac{d\delta_1}{dt} = \frac{(\delta_3 - \alpha_S - \delta_1)}{S_1} F_{31} \quad (12)$$

Similarly,

$$\frac{d\delta_2}{dt} = \frac{(\delta_3 - \delta_2)}{S_2} F_{32} \quad (13)$$

$$\frac{d\delta_5}{dt} = \frac{(\delta_4 - \alpha_C - \delta_5)}{C_5} F_{45} \quad (14)$$

$$\frac{d\delta_6}{dt} = \frac{(\delta_4 - \delta_6)}{C_6} F_{46} \quad (15)$$

Given some initial conditions (that is values for S_i , $i = 1 - 7$ and for δ_i , $i = 1 - 6$), eqs (1) to (4), (7), and (8) to (15) can be used to obtain the time evolution of the system.

$\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ values for the ocean (figs. 2 and 3) are taken from the compilation by Lindh (1983), except as modified recently by the data of Popp, Anderson, and Sandberg (1986) and Arthur, Dean, and Claypool (1985). Initial values and k 's are given in table 1.

TABLE 1

$k_{13} = 0.00267$	$k_{23} = 0.00534$
$k_{54} = 0.004$	$k_{64} = 0.004$
$S_1 = 250$	$S_2 = 250$
$S_3 = 40$	$C_4 = 2.8$
$C_5 = 1250$	$C_6 = 5000$
$\delta_1 = -10$	$\delta_2 = 20$
$\delta_5 = -20$	$\delta_6 = 2$
$\alpha_S = 35$	$\alpha_C = 25$

k 's in my^{-1} ; S 's and C 's in 10^{18} moles; δ and α in permil.

At this point it is important to address the use of eqs (3) and (4) in the various isotope models. While eqs (1) and (2) are correct if the oceans are at steady state, eqs (3) and (4) are only *approximate*; the correct equations (which assume that the ratio of heavy to light isotope abundances is much less than one—a very good assumption. See also eq (7) in Holland, 1973, for a rigorous derivation relating $d\delta/dt$ and

$d(^{34}\text{S}/^{32}\text{S})/dt$) are analogous to eqs (12) to (15), that is

$$S_3 \frac{d\delta_3}{dt_{\text{meas}}} = (\delta_1 - \delta_3)F_{13} + (\delta_2 - \delta_3)F_{23} + \alpha_S F_{31} \quad (16)$$

$$C_4 \frac{d\delta_4}{dt_{\text{meas}}} = (\delta_5 - \delta_4)F_{54} + (\delta_6 - \delta_4)F_{64} + \alpha_C F_{45} \quad (17)$$

Eqs (16) and (17) use the measured *variation* in $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ as well as the δ values themselves to constrain the fluxes. To obtain well-defined derivatives, the data in figures 2 and 3 were fitted to a high order Fourier series (40 terms). The resulting δ_i are given in figures 4 and 5.

In addition, we should allow for variation in the sulfate and bicarbonate reservoirs, that is, under non-steady state oceanic conditions eqs (1) to (2) become:

$$\frac{dS_3}{dt_{\text{input}}} = F_{13} + F_{23} - F_{31} - F_{32} \quad (18)$$

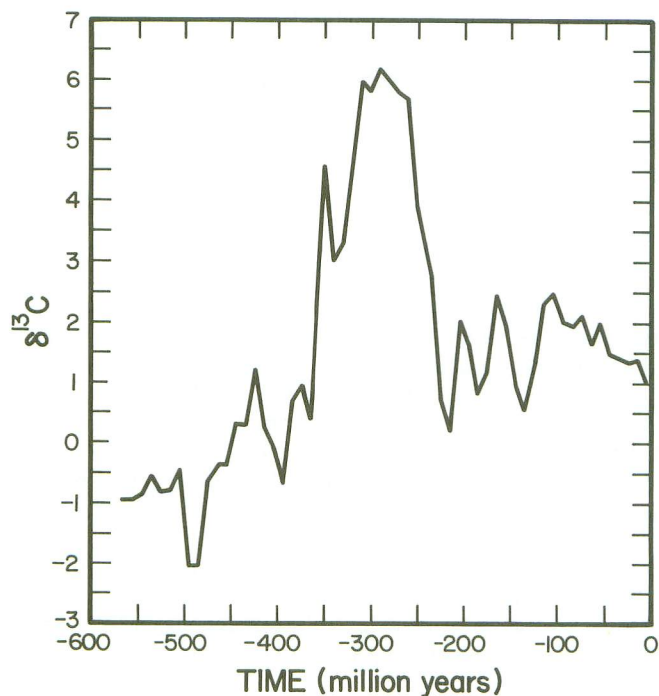


Fig. 2. $\delta^{13}\text{C}$ ocean data for the Phanerozoic from Lindh (1983), Arthur, Dean, and Claypool (1985) and Popp, Anderson, and Sandberg (1986).

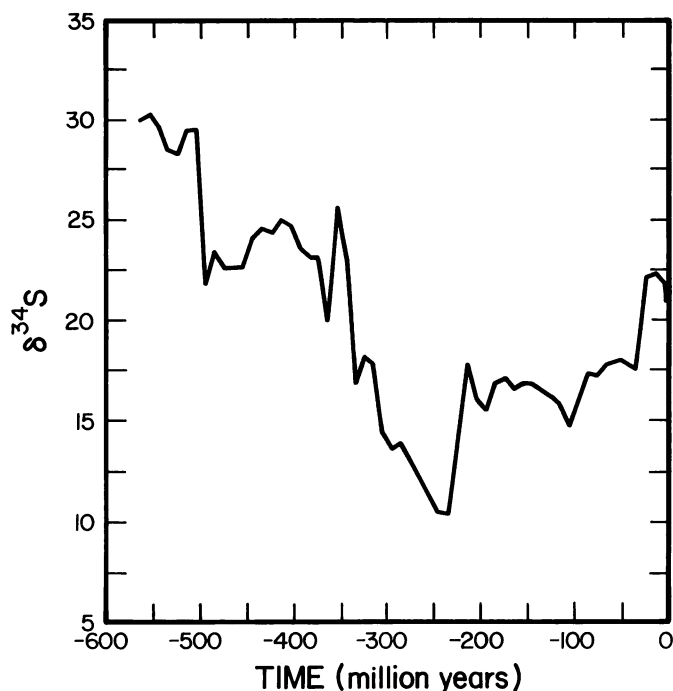


Fig. 3. $\delta^{34}\text{S}$ ocean data for the Phanerozoic from Lindh (1983), Arthur, Dean, and Claypool (1985), and Popp, Anderson, and Sandberg (1986).

$$\frac{dC_4}{dt}_{\text{input}} = F_{54} + F_{64} - F_{45} - F_{46} \quad (19)$$

Figure 6 gives the results for the burial rate of organic matter and the burial rate of pyrite using the traditional set of equations, that is, eqs (1) to (4), (7), and (8) to (15). We can compare these results with those in figure 7, which used the correct eqs (1) and (2), (16) and (17), and (7), (8) to (15). While it is clear that the approximation inherent in eqs (3) and (4) are very good for the carbon isotopes (due to the small amount of HCO_3^- in the oceans), they are *not* good for the sulfur isotopes. In particular, the “correct” solution shows much more marked fluctuations in the rate of pyrite burial. Future models of the sulfur cycle should really use eqs (16) and (17), which properly input the *rate of change* of the isotopic values as well as the values themselves into the time evolution calculations. We will use only eqs (16) and (17) in the rest of the paper.

THE OXYGEN CATASTROPHE

The results in figures 6 and 7 can be used to show clearly what may be termed the “oxygen catastrophe.” If we incorporate the results from

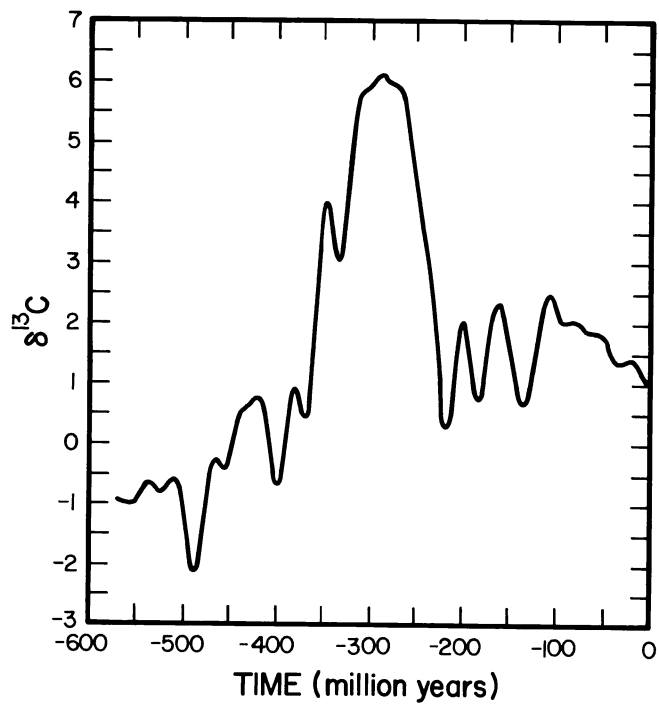


Fig. 4. Fourier fit of the $\delta^{13}\text{C}$ data in figure 2. An equation of the form $\delta = \sum_{i=1}^{40} A_i \cos(((i-1)\pi/570)t)$ is used.

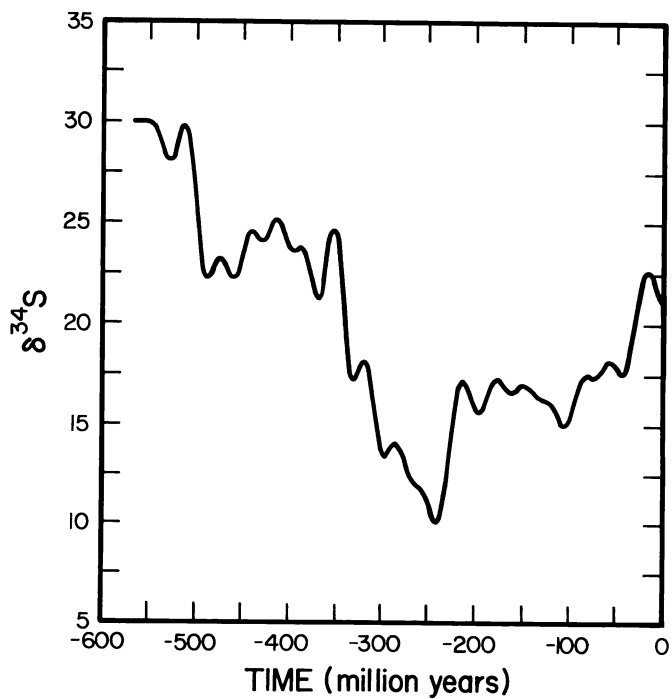


Fig. 5. Fourier fit of the $\delta^{34}\text{S}$ data in figure 3. An equation of the form $\delta = \sum_{i=1}^{40} A_i \cos(((i-1)\pi/570)t)$ is used.

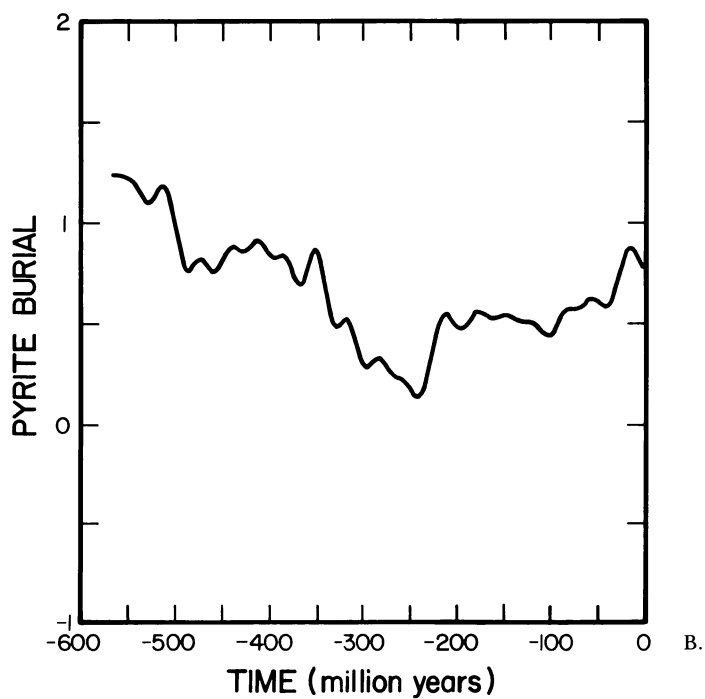
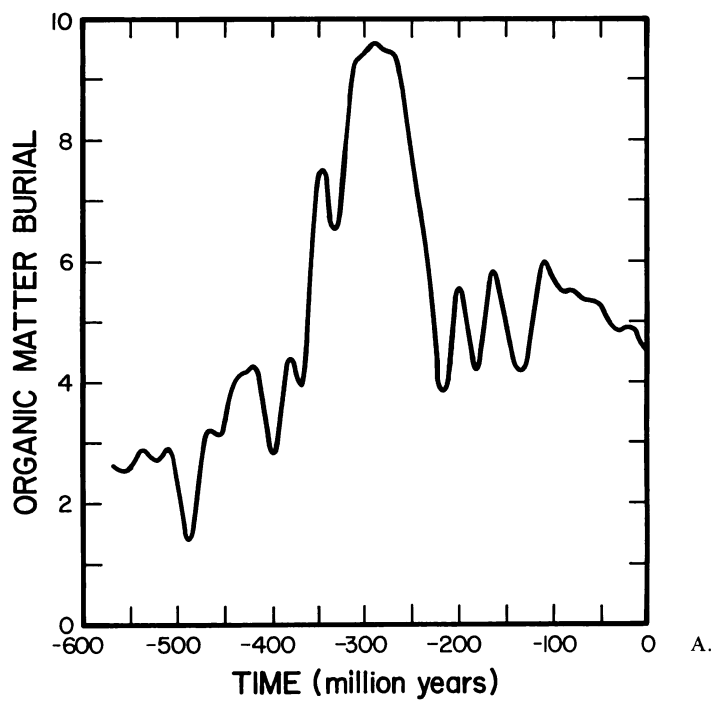


Fig. 6. Model results using the usual eqs (3) and (4) for the isotope mass balance. (A) organic matter burial rate; (B) pyrite burial rate (in 10^{18} moles/my).

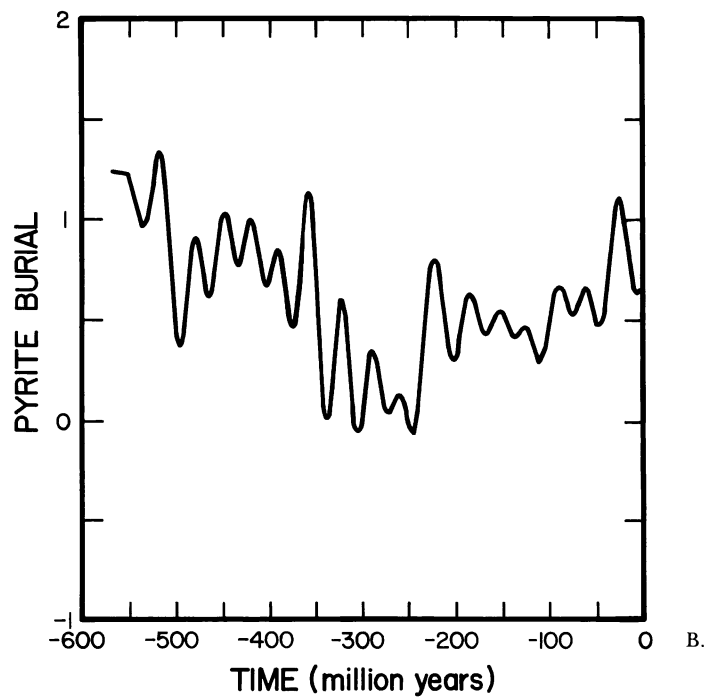
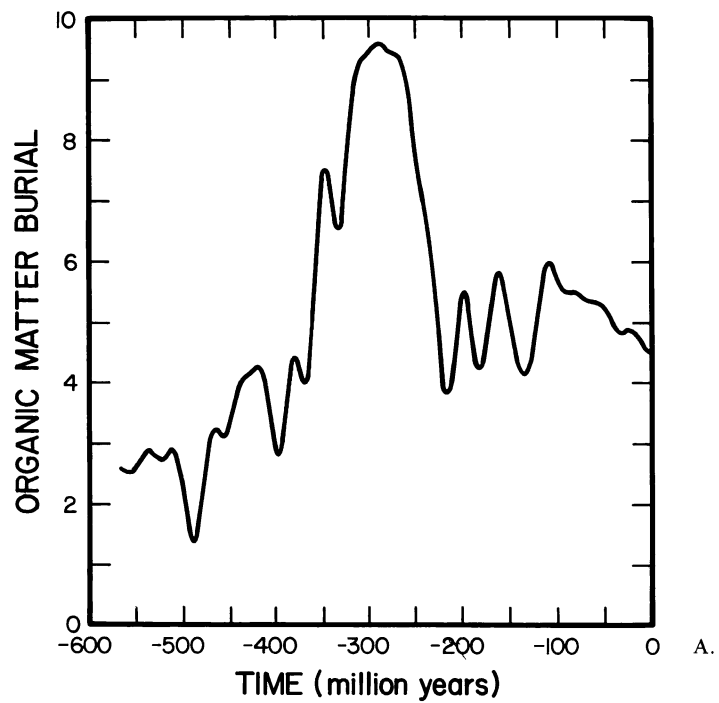


Fig. 7. Model results using the correct eqs (16) and (17) for the isotope fluxes into the oceans. (A) organic matter burial rate; (B) pyrite burial rate (in 10^{18} moles/my).

the C and S flux calculations into eq (7), we can calculate the variation of O_2 predicted by the weathering and depositional fluxes. The predicted oxygen content of the atmosphere behaves in an unwieldy manner, with both negative values and very high values predicted as shown in figure 8! An obvious problem with this method is the lack of adequate feedbacks into the oxygen geochemical cycle. Herein we arrive at a knotty problem. Unknown feedbacks in the carbon and sulfur cycles have been handled by the isotope model; but now we are left with deciphering the dynamics of a third element. One solution would be to introduce a negative feedback into the flux, F_{54} , stemming from the oxidation (weathering) of organic carbon. Disregarding tectonic questions for the time being, let eq (14) for the flux, F_{54} , be modified to

$$F_{54} = k_{54} \frac{S_{O_2}}{S_{O_2}^o} S_5 \quad (20)$$

where S_{O_2} is the mass of oxygen in the atmosphere at time t and $S_{O_2}^o$ is the present-day mass of oxygen. Eq (20) (Kump and Garrels, 1986) postulates the reasonable theorem that increasing the oxygen content of the atmosphere increases the rate of oxidative weathering of organic carbon. Eq (20) would be expected to add a negative feedback and dampen the O_2 fluctuations in figure 8. Instead, we obtain the surprising results show in figure 9. The feedback has, in fact, become a positive feedback in places (see also Berner, 1987). The explanation for this paradox stems from the incompatibility of a strictly dynamic feedback and an externally driven isotope model. To understand the problem, imagine (see fig. 1) that for some reason there is an increase in the organic carbon burial rate. This increase would lead to an increase in atmospheric O_2 . Therefore, the feedback in eq (20) responds by increasing the rate of organic matter weathering (and so the rate of uptake of oxygen). However, this increases the input of light isotopic carbon to the oceans. Because the oceans must maintain a given $\delta^{13}C$ value, the isotope model prescribes a bigger *increase* in the organic carbon burial rate! The net result is an increase in the rate of oxygen production and a positive feedback.

A resolution of the oxygen catastrophe is not simple. One solution, that is not particularly satisfying, is to incorporate the oxygen feedback (eq 20) into the rate equation for oxygen but leave the feedback out of the isotope model. Such a modified procedure does yield reasonable results as can be seen in figure 10 (see also Berner, 1987). Nonetheless, we obviously need a better resolution of this problem. The solution must come from one of two directions. The better approach would be to forego the isotope model and have completely dynamic equations for the C–O–S cycles in the Earth. This approach would have to predict the interactions between nutrients and net productions of pyrite and organic carbon in sediments as well as the feedback between oxygen and all the fluxes. While this approach is clearly the most correct, it is quite

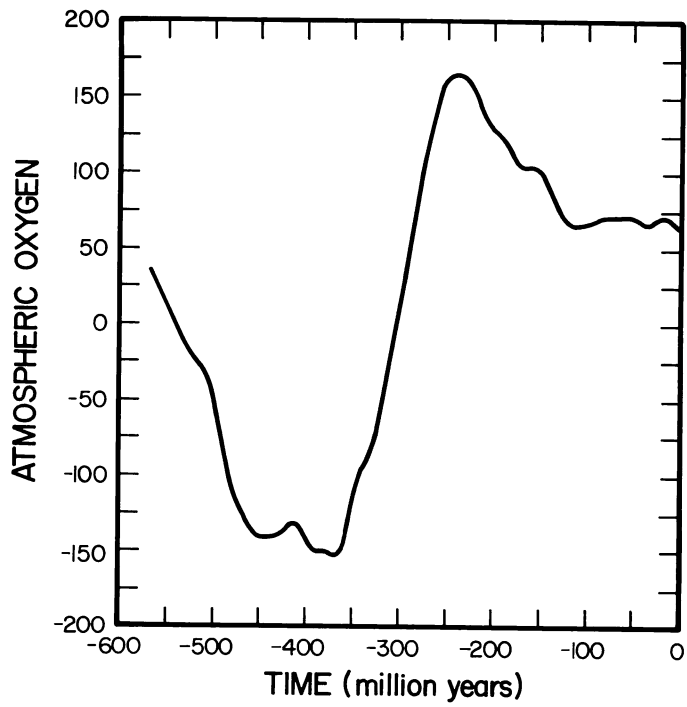


Fig. 8. Atmospheric oxygen variations predicted by the fluxes calculated in figure 7 (in 10^{18} moles).

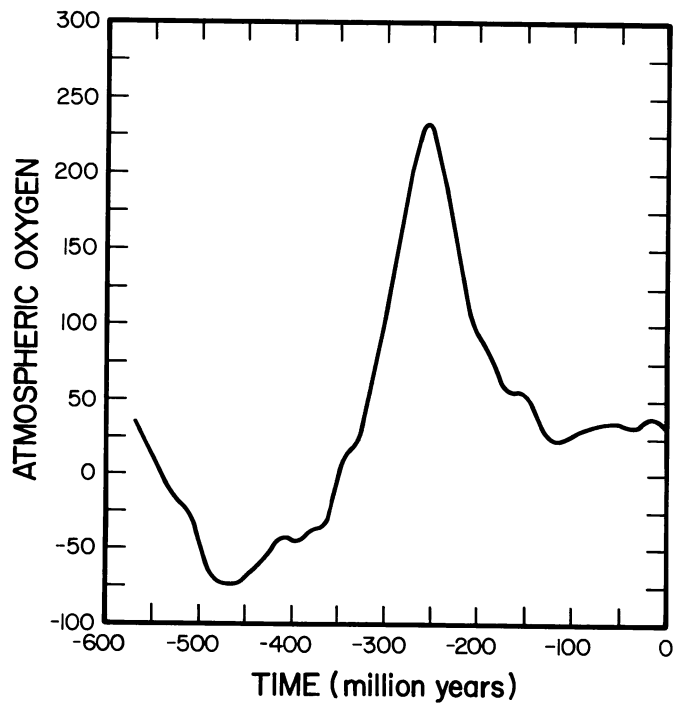


Fig. 9. Atmospheric oxygen variations predicted using the isotope model but making the weathering rates depend on the oxygen level as in eq (20) (in 10^{18} moles).

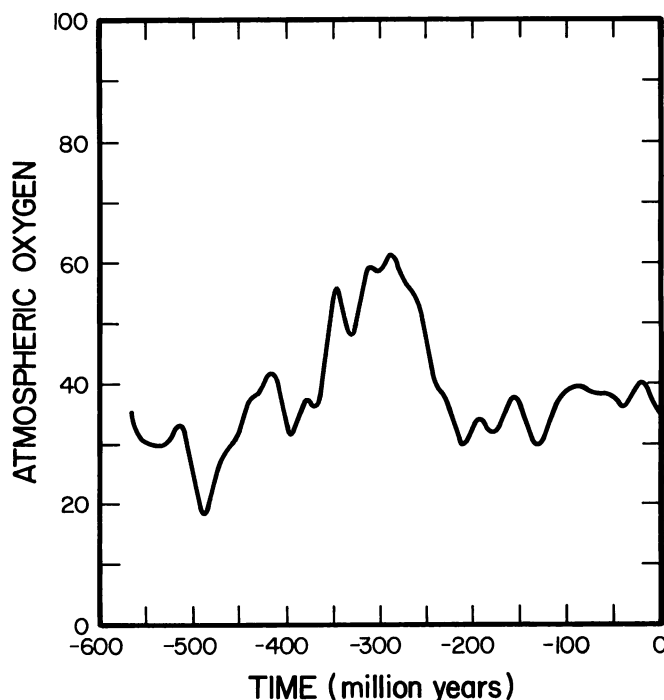


Fig. 10. Atmospheric oxygen variations predicted using the isotope model but adding an oxygen feedback (eq 20) only in eq (7) for the evolution of oxygen (in 10^{18} moles).

intractable at the present time. The alternative route is to improve on the isotope model, that is, work out a solution within the predictive scheme embodied in the isotope model. To do this we need a much more general method that enables many different flux and mass balance relations or constraints to be handled. The next section discusses such a model.

STATISTICAL ISOTOPE MODEL

The new method proposed in this section not only handles the added constraints discussed above but also allows us to check whether the isotopic data and the overall geochemical cycle are consistent. The basic premise is to recognize that the eqs (1), (2), (16), (17) are driven by data that have some error bounds and that the equations themselves are but an approximation to the dynamics of a complex system. For example, we have simplified the geochemical cycle; therefore, leaks into or out of the system (such as from the mantle) will upset the mass balance calculations. At the same time, the oxygen catastrophe arises because the condition that $dS_{O_2}/dt \approx 0$ is far from being satisfied. Again, within

some general bounds, we expect that dS_{O_2}/dt will not deviate significantly from zero. Likewise, we should add that the constancy of the fractionation factors, α in eqs (16) and (17), is again subject to fluctuations (Popp and other, this issue). The fluctuations in the data, the validity of the equations, and the uncertainty in the α 's necessitate a statistical approach.

To proceed further we can define the following expressions, A_i :

$$A_1 = F_{13} + F_{23} - F_{31} - F_{32} - \frac{dS_3}{dt} \sim 0 \quad (21)$$

$$A_2 = F_{54} + F_{64} - F_{45} - F_{46} - \frac{dC_4}{dt} \sim 0 \quad (22)$$

$$A_3 = (\delta_1 - \delta_3)F_{13} + (\delta_2 - \delta_3)F_{23} + \alpha_S F_{31} - S_3 \frac{d\delta_3}{dt_{\text{meas}}} \sim 0 \quad (23)$$

$$A_4 = (\delta_5 - \delta_4)F_{54} + (\delta_6 - \delta_4)F_{64} + \alpha_C F_{45} - C_4 \frac{d\delta_4}{dt_{\text{meas}}} \sim 0 \quad (24)$$

$$A_5 = F_{45} + \frac{15}{8} F_{31} - \frac{15}{8} F_{13} - F_{54} \sim 0 \quad (25)$$

$$A_6 = \alpha_S - \alpha_S^0 \sim 0 \quad (26)$$

$$A_7 = \alpha_C - \alpha_C^0 \sim 0 \quad (27)$$

where α_S^0 and α_C^0 refer to their present-day values.

We would like, ideally, to have all the A_i be near zero. However, this is an overdetermined system. Instead, the proper approach is to enforce the eq $A_i = 0$ with different degrees of severity. We can incorporate the severity in a statistical weight, w_i . Therefore, we construct the function J :

$$J = \sum_i w_i A_i^2 \quad (28)$$

The proper evolution of the system is now obtained by always minimizing the function J . The independent variables in such a minimization (see app.) are F_{31} , F_{32} , F_{45} , F_{46} , α_S , and α_C . Minimization of J with respect to four of these variables leads to the equations:

$$\frac{\partial J}{\partial F_{31}} = 0 \quad (29)$$

$$\frac{\partial J}{\partial F_{45}} = 0 \quad (30)$$

$$\frac{\partial J}{\partial \alpha_S} = 0 \quad (31)$$

$$\frac{\partial J}{\partial \alpha_C} = 0 \quad (32)$$

The minimization of J with respect to the other two variables, F_{32} and F_{46} , that is, eqs

$$\frac{\partial J}{\partial F_{32}} = 0$$

$$\frac{\partial J}{\partial F_{46}} = 0$$

produces the *same* equations as eqs (18) and (19) (see app.). Therefore, after computing F_{31} and F_{45} (see below), the values of F_{32} and F_{46} are determined by the steady state or non-steady-state nature of sulfate and bicarbonate in the oceans, that is, the size of dS_3/dt and dC_4/dt in eqs (18) and (19). It is interesting that when the proper equations are used for the changes in δ (for example, eqs 16 and 17), the non-steady state nature of oceanic sulfate or bicarbonate *does not directly* affect the burial fluxes of the reduced species. In other words, the calculation of F_{31} at any step in the model gives the same number regardless of whether dS_3/dt is zero or not! The size of dS_3/dt just affects the calculation of F_{32} via eq (18).

The four equations in the minimization of J (eqs 29, 32) produce four relations that can be used to solve for F_{31} , F_{45} , α_S , and α_C :

$$w_3 A_3 \alpha_S + \frac{15}{8} w_5 A_5 = 0 \quad (33)$$

$$w_4 A_4 \alpha_C + w_5 A_5 = 0 \quad (34)$$

$$w_3 A_3 F_{31} + w_6 A_6 = 0 \quad (35)$$

$$w_4 A_4 F_{45} + w_7 A_7 = 0 \quad (36)$$

These four equations can be solved for the four unknowns once values are given to the five weights (w_3 , w_4 , w_5 , w_6 , w_7). Note that the weights for A_1 and A_2 (w_1 and w_2) do *not* enter into the calculations, for the same reason that the fluxes, F_{32} and F_{46} , are independently calculated by eqs (18) and (19). In what follows we only give the values of the five weights w_3 thru w_7 . Note also that in solving eqs (33) to (36), we must insert the algebraic expressions for the A_i given by eqs (21) to (27), expressions

which include the unknown variables we are trying to solve for. For example, eq (33) really stands for the equation:

$$w_3 \left((\delta_1 - \delta_3) F_{13} + (\delta_2 - \delta_3) F_{23} + \alpha_S F_{31} - S_3 \frac{d\delta_3}{dt_{\text{meas}}} \right) \alpha_S + \frac{15}{8} w_5 \left(F_{45} + \frac{15}{8} F_{31} - \frac{15}{8} F_{13} - F_{54} \right) = 0$$

which contains the unknowns, F_{31} , F_{45} , and α_S . Having obtained values for F_{31} , F_{45} , α_S , and α_C from eqs (33) to (36), new values of the time derivatives appearing in eqs (7) to (15) are computed, and these are used to obtain new values of S_1 , S_2 , S_3 , C_4 , C_5 , C_6 , S_{O_2} and δ_1 , δ_2 , δ_5 , δ_6 for the next time step. Because this new approach enables fluctuations from the “measured” values, the calculated value of $d\delta_3/dt$ and $d\delta_4/dt$ will not be the same as the values input from the data (that is, to make up A_3 and A_4). Thus, once the fluxes are computed as indicated above, they are inserted into eqs (16) and (17) to calculate the actual time derivatives in the dynamics. It is *these* derivatives that are used to obtain the updated values of δ_3 and δ_4 , which may not agree precisely with the measured values (see figs. below). This process is repeated for each time step in the overall integration of the model (see app. for more details).

All previous models can be considered as subsets of this new general model. For example, the earlier results of figure 6 represent the case where the w_i (recall only w_3 to w_7 are relevant) are given by (1, 1, 0, 1, 1) and where the sulfate and bicarbonate reservoirs are assumed to be at steady state. However, the following figures will illustrate the power of the new method in circumventing the oxygen catastrophe as well as in providing a new avenue for carrying out geochemical model calculations beyond those considered here.

Figure 11 gives the model results for the arbitrary case of $\vec{w} = (1, .001, .01, .01, .1)$. The reader should refer to eqs (21) to (27) for the definitions of A_i . It should also be noted that the higher the value of w_i , the more tightly the corresponding A_i is constrained to equal zero. Figure 11 shows that now a well behaved oxygen curve is obtained without the necessity to invoke inconsistent correction factors. There is still a significant increase in atmospheric oxygen at the Permo-Carboniferous period. There is negligible variation from the measured $\delta^{34}S$ curve (in fact although the two curves are plotted in the figure, they are indistinguishable) and in the fractionation factor α_S . However, the carbon system shows bigger variations. The biggest variation in $\delta^{13}C$ stems from the high Popp data centered around 300 my ago. The model decreases the $\delta^{13}C$ values while still maintaining a high peak in the Carboniferous. The deviations in α_C are modest with the biggest departure occurring in the Carboniferous and the Ordovician. The pyrite burial rate is very close to that in figure 7B, reflecting the negligible changes in $\delta^{34}S$ and α_S . However, the organic matter burial rate has now changed significantly, with a reduced peak at the Carboni-

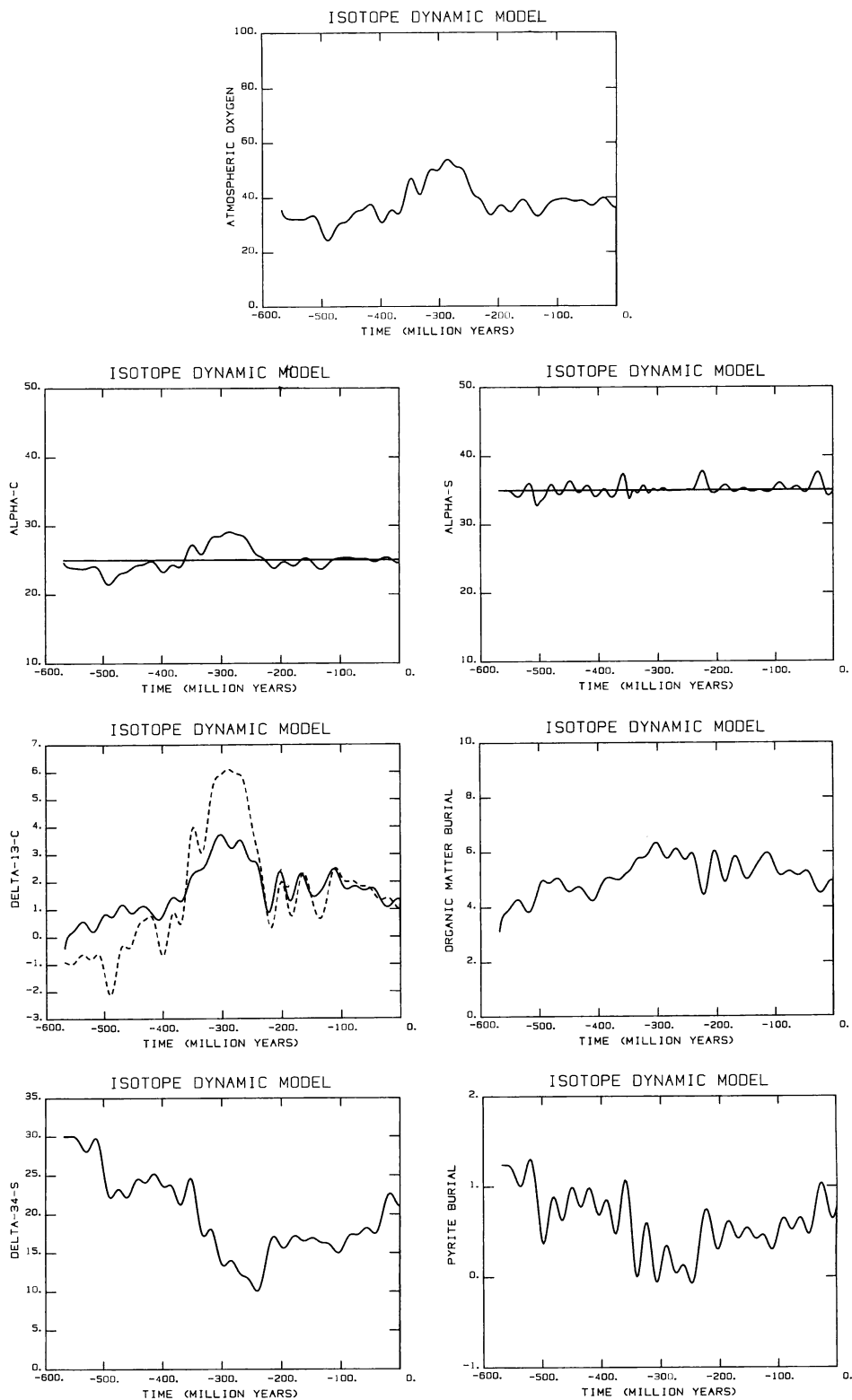


Fig. 11. Model results using the statistical method and a $\bar{w} = (1, 0.001, 0.01, 0.01, 0.1)$. Steady state is assumed for HCO_3^- and SO_4^{2-} . All fluxes are in 10^{18} moles/my. All contents are in 10^{18} moles.

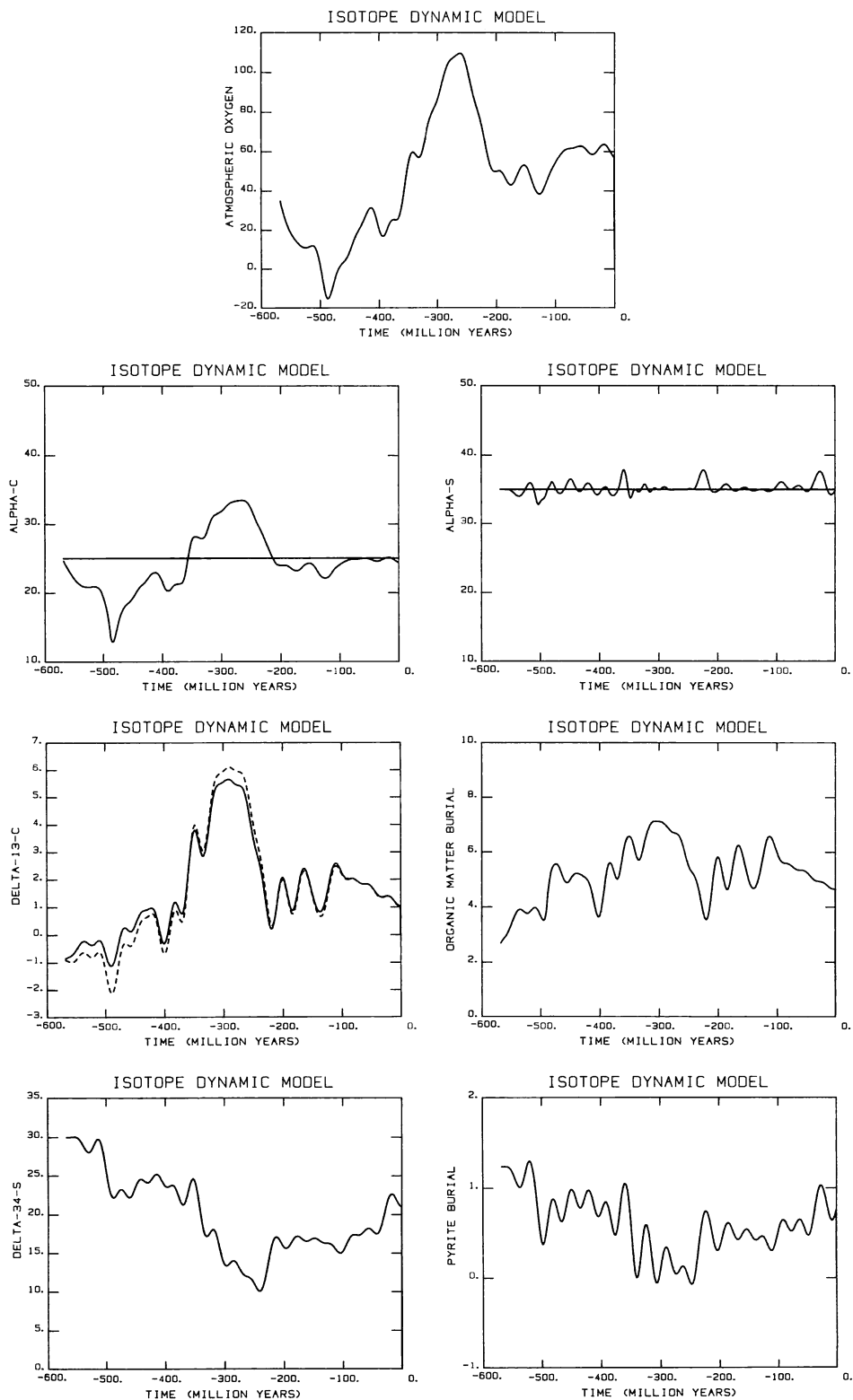


Fig. 12. Model results using the statistical method and a $\vec{w} = (1, 0.01, 0.01, 0.01, 0.1)$. Steady state is assumed for HCO_3^- and SO_4^{2-} . All fluxes are in 10^{18} moles/my. All contents are in 10^{18} moles.

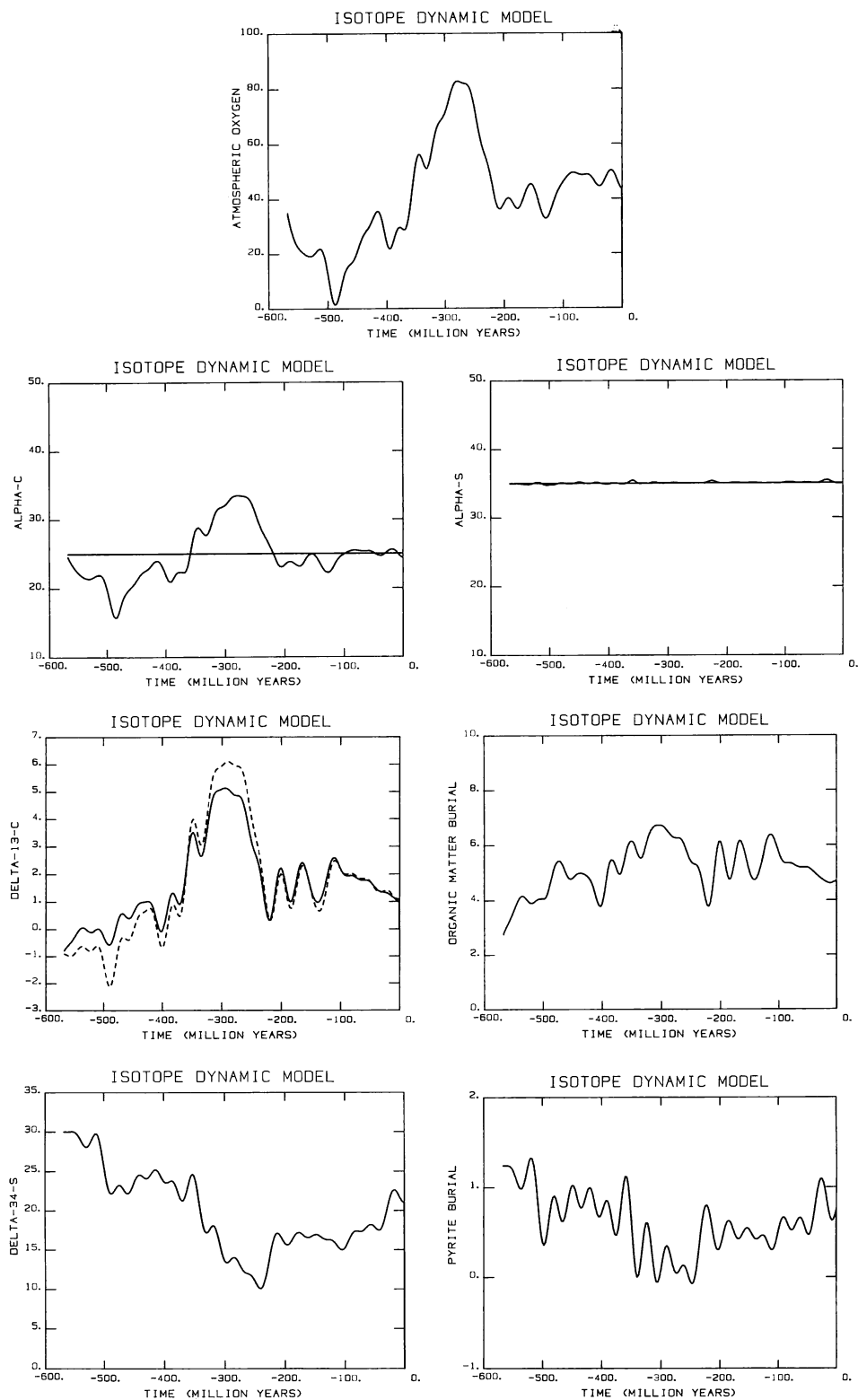


Fig. 13. Model results using the statistical method and a $\vec{w} = (0.1, 0.005, 0.01, 0.01, 0.1)$. Steady state is assumed for HCO_3^- and SO_4^{2-} . All fluxes are in 10^{18} moles/my. All contents are in 10^{18} moles.

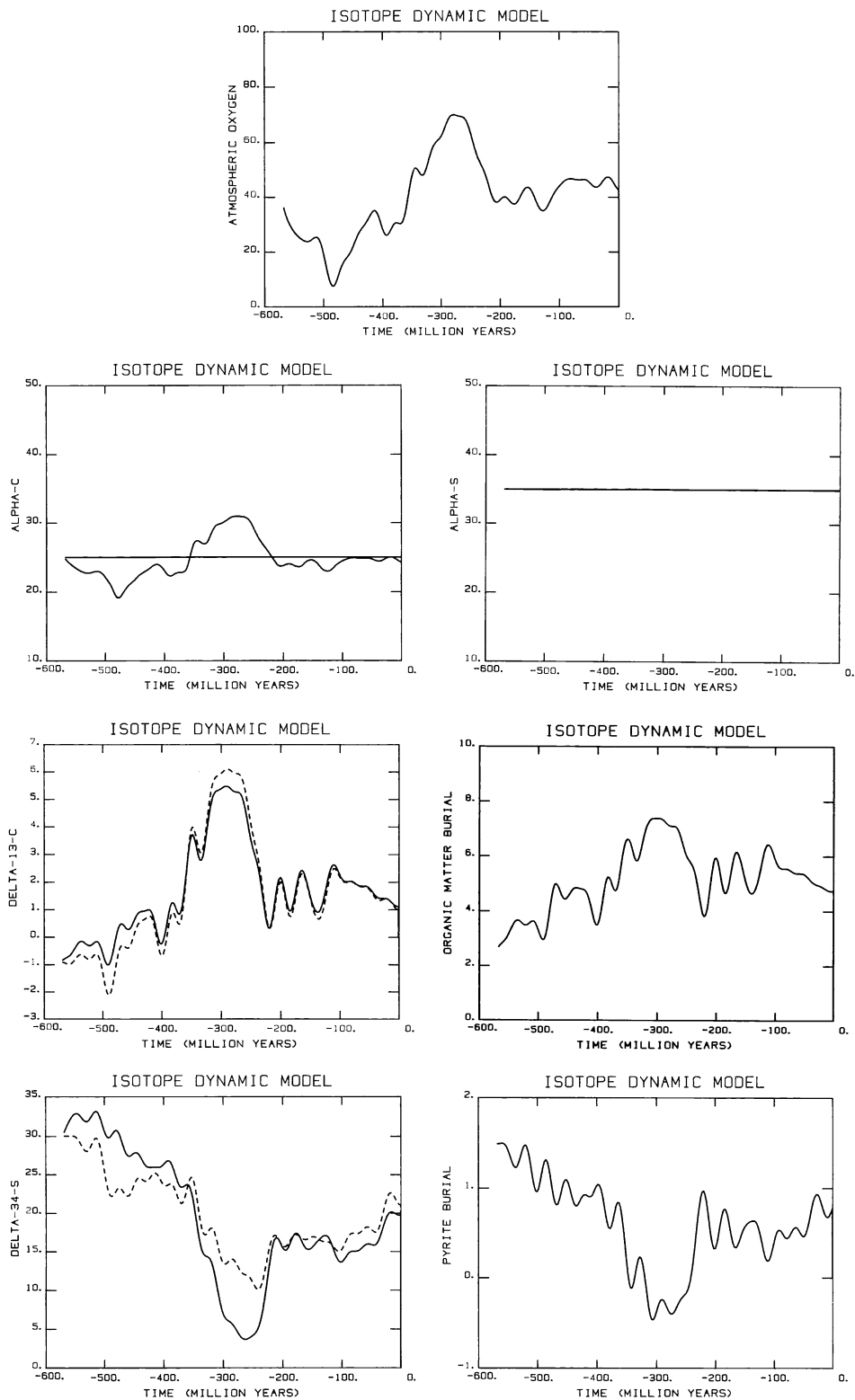


Fig. 14. Model results using the statistical method and a $\vec{w} = (0.00005, 0.005, 0.01, 0.01, 0.1)$. Steady state is assumed for HCO_3^- and SO_4^{2-} . All fluxes are in 10^{18} moles/my. All contents are in 10^{18} moles.

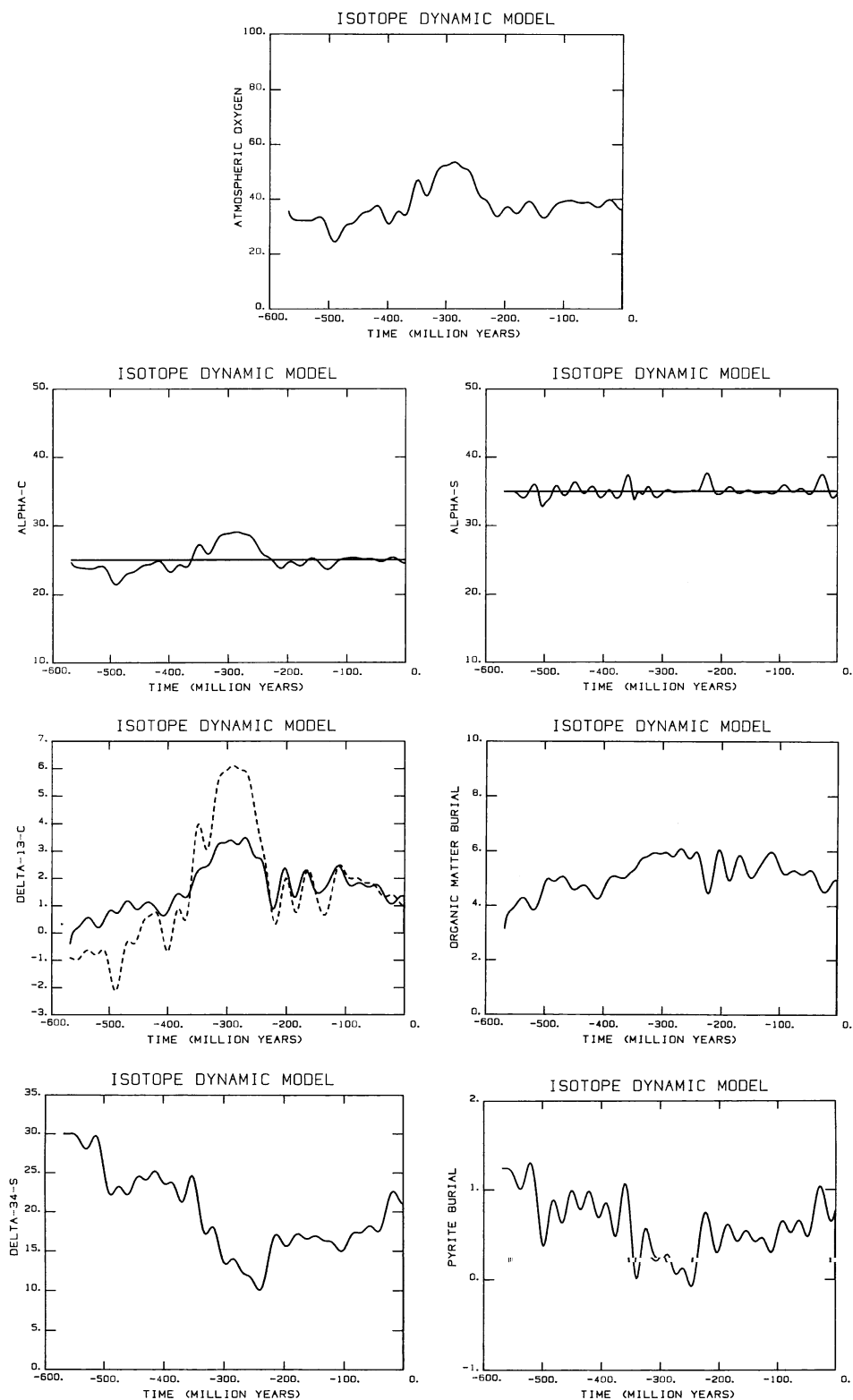


Fig. 15. Model results using the statistical method, a $\bar{w} = (1, 0.001, 0.01, 0.01, 0.1)$ and a ocean sulfate variation given in eq (37) with $A = -35$, $t_o = -300$, and $\sigma = 20$ my.

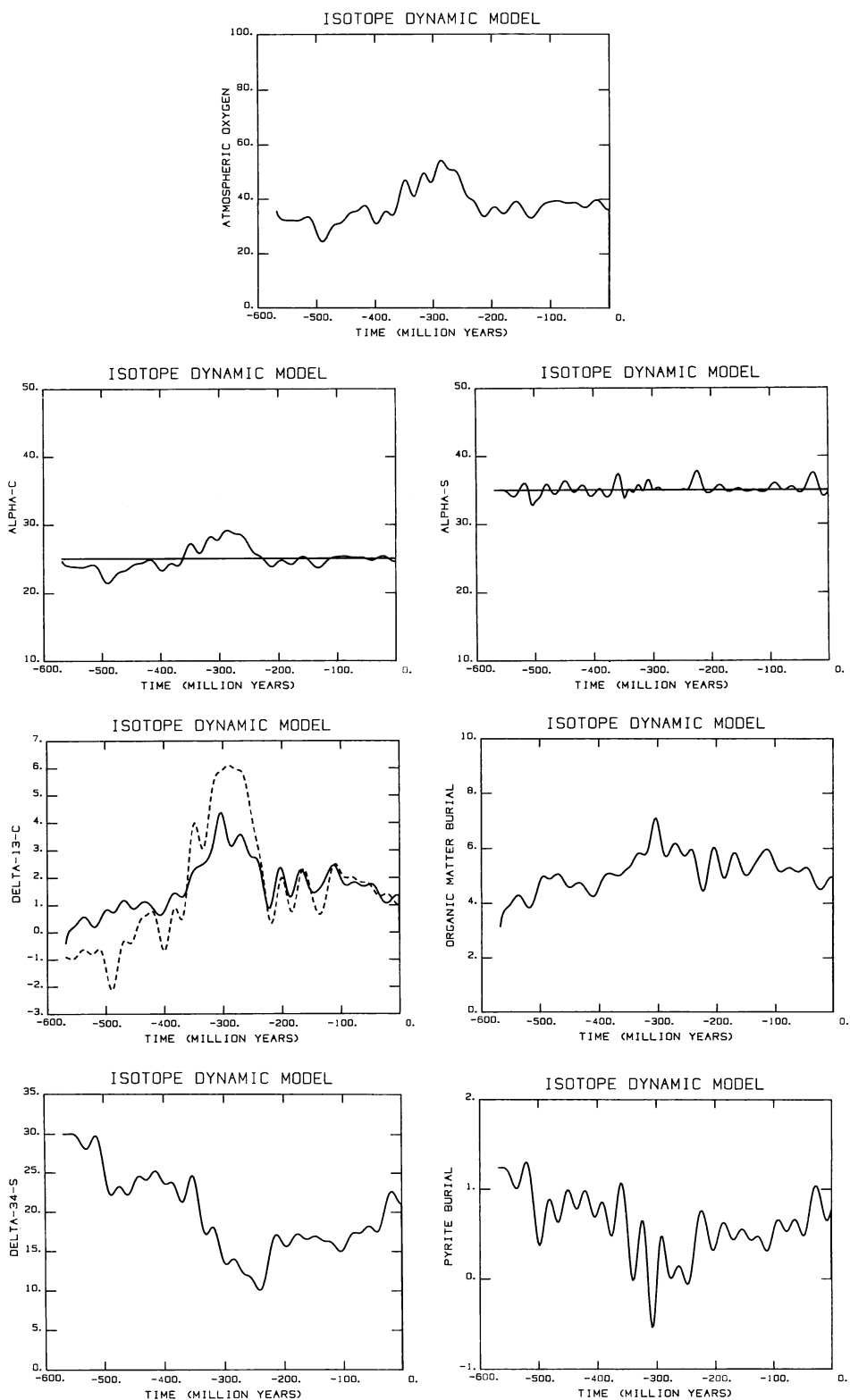


Fig. 16. Model results with the same parameters as in figure 15 but with $A = +60$.

ferous. Note that the C/S ratio is still quite high at the Carboniferous (Berner, 1987).

Figures 12 to 14 illustrate the changes in the model results as a function of variations in $\vec{w}$. In figure 12 we have changed $\vec{w}$ to (1, .01, .01, .01, .1), increasing adherence to the $\delta^{13}\text{C}$ values. As a result the $\delta^{13}\text{C}$ curve is now quite close to the measured curve; however, the calculated oxygen curve contains unacceptable variations, and the α_c curve also has begun to fluctuate significantly.

Figure 13 improves the results of figure 12 by compromising to a value of $\vec{w} = (0.1, .005, .01, .01, .1)$. The effects of varying the $\delta^{34}\text{S}$ values is shown in figure 14, which differs from the previous figure by having $\vec{w} = (0.00005, 0.005, .01, .01, .1)$. Note that now the oxygen curve is improved, and the carbon isotope curve is closer to the "measured" at the expense of the sulfur isotope curve.

Up to now the calculations have all assumed steady state for sulfate (S_3) and bicarbonate (S_4) in the oceans. We can explore the effects of allowing sulfate to vary by using the following S_3 curve:

$$\text{S}_3 = \text{S}_3^0 + A e^{-(t-t_0)^2/\sigma^2} \quad (37)$$

where the amplitude of the variation is controlled by A and the duration by σ . Figure 15 gives the results for the case where $A = -35$, $t_0 = -300$, and $\sigma = 20$ my. In this case the sulfate content of the oceans would be significantly decreased during the Carboniferous period (see fig. 15). The rest of the calculation assumes $w = (1, 0.001, .01, .01, .1)$, which corresponds to figure 11. Comparing figures 15 and 11, we see that the effect on the oxygen curve is a modest one, with bigger effects on the organic matter burial rate and the pyrite burial rate curves. Figure 16 illustrates the case of a sulfate increase for 40 my during the Carboniferous, that is, $A = +60$, $t_0 = -300$, and $\sigma = 20$ my. The effect is bigger in this case. Overall, the nonsteady-state nature of sulfate will quantitatively modify the predicted profiles; however, varying sulfate by itself will not alleviate the constraint problems nor solve the oxygen catastrophe.

SUMMARY

This paper has addressed two important points. First, the proper use of eq (16) in isotope models leads to non-trivial changes in the calculated sulfur fluxes. These equations have not been generally used in past isotope models. Second, spurred by the oxygen catastrophe, the input of constraints or upper/lower bounds on geochemical cycles is an important feature that has been neglected in the past. Such constraints are required because the systems are generally underdetermined and the data (for example, isotope data) are not precise. Given these conditions, illustrated by the oxygen catastrophe, the expansion of the usual models to include bounds and constraints is a logical one. The use of the statistical approach in this paper initiates such an expansion. Nonetheless, the ideas presented here can be elaborated much further, and it is hoped that future research will do just that.

APPENDIX

In this appendix we outline in more detail the workings of the statistical approach. In solving the dynamics of the redox cycles, the weathering fluxes are usually assumed “known,” see eqs (8) to (11). Therefore, the unknown fluxes in our system are the burial fluxes or F_{31} , F_{32} , F_{45} , and F_{46} . In addition, if we allow for fluctuations in the fractionation parameters, α_S and α_C will also become unknowns. Note that if we specify these six unknowns (4 fluxes and the two α ’s) at any given time, then eqs (7) and (12) to (15) will immediately yield values of dS_{O_2}/dt and $d\delta_i/dt$, and these derivatives will yield the values of S_{O_2} and δ_i at the next time step. Likewise equations such as

$$\frac{dS_1}{dt} = F_{31} - F_{13}$$

will yield values of dS_1/dt , dS_2/dt , dC_5/dt , and dC_6/dt . These derivatives will now enable new values of S_1 , S_2 , C_5 , and C_6 to be computed for the next time step. Finally S_3 and C_4 are updated according to the particular steady or non-steady-state input function, that is, $S_3(t)$ and $C_4(t)$ are either constant or must be independently given in the correct isotope model. Therefore, once the six unknowns are obtained, the rest of the system can be evaluated at the next time step.

The dynamics of the system depend on the values of the six unknown mentioned above. Therefore, our function, J , will also be some function of these six unknowns, that is,

$$J = J(F_{31}, F_{32}, F_{45}, F_{46}, \alpha_S, \alpha_C)$$

If we require that J be always a minimum throughout the dynamics or evolution of the redox cycles, then six equations are obtained. These six equations stem from the mathematical requirement that a minimum be a stationary point (zero slope). Thus, for each unknown F or α we must have

$$\frac{\partial J}{\partial F} = 0$$

$$\frac{\partial J}{\partial \alpha} = 0$$

At this point, one would expect to solve 6 simultaneous (non-linear) equations in six unknowns. However, as pointed out in the text, two of these equations reduce to (18) and (19). To see this, evaluate

$$\frac{\partial J}{\partial F_{32}} = \sum_i 2w_i A_i \frac{\partial A_i}{\partial F_{32}} = 0 \quad (A-1)$$

where we used the definition of J (eq 28) and the sum is over the seven A_i . The derivative is set equal to zero because of the zero slope requirement. To compute the derivatives we use the definitions of A_i given in (21) to (27). This yields

$$\frac{\partial J}{\partial F_{32}} = 2w_1 A_1 (-1) = 0 \quad (A-2)$$

because only A_1 contains the unknown F_{32} . Obviously the result of minimizing J with respect to F_{32} is the same as requiring at all times that

$$A_1 = 0 \quad (A-3)$$

Similarly, minimization with respect to F_{46} requires that A_2 be zero. This interesting result states that eqs (18) and (19) (A_1 and $A_2 = 0$) solely determine F_{32} and F_{46} .

This leaves the other four unknowns. The equations obtained when eq (A-1) is applied to these four unknowns are the ones given in the text as (33) to (36) (Note the common factor of 2 has been cancelled out in these equations). To solve these equations, we must insert the expressions for the A_i . Thus eqs (33) to (36) are really a short-hand notation for the equations:

$$w_3 \left((\delta_1 - \delta_3)F_{13} + (\delta_2 - \delta_3)F_{23} + \alpha_S F_{31} - S_3 \frac{d\delta_3}{dt_{\text{meas}}} \right) \alpha_S + \frac{15}{8} w_5 \left(F_{45} + \frac{15}{8} F_{31} - \frac{15}{8} F_{13} - F_{54} \right) = 0 \quad (\text{A-4})$$

$$w_4 \left((\delta_5 - \delta_4)F_{54} + (\delta_6 - \delta_4)F_{64} + \alpha_C F_{45} - C_4 \frac{d\delta_4}{dt_{\text{meas}}} \right) \alpha_C + w_5 \left(F_{45} + \frac{15}{8} F_{31} - \frac{15}{8} F_{13} - F_{54} \right) = 0 \quad (\text{A-5})$$

$$w_3 \left((\delta_1 - \delta_3)F_{13} + (\delta_2 - \delta_3)F_{23} + \alpha_S F_{31} - S_3 \frac{d\delta_3}{dt_{\text{meas}}} \right) F_{31} + w_6 (\alpha_S - \alpha_S^0) = 0 \quad (\text{A-6})$$

$$w_4 \left((\delta_5 - \delta_4)F_{54} + (\delta_6 - \delta_4)F_{64} + \alpha_C F_{45} - C_4 \frac{d\delta_4}{dt_{\text{meas}}} \right) F_{45} + w_7 (\alpha_C - \alpha_C^0) = 0 \quad (\text{A-7})$$

The reader will note that these four equations are non-linear (terms such as $\alpha_S^2 F_{31}$ are present). However, the first two equations are linear in the two unknowns F_{31} and F_{45} . The latter two equations are linear in α_S and α_C . Therefore, in practice what was carried out is an iterative scheme. The first two equations are used to solve for new values of F_{31} and F_{45} (using the old values for α_S and α_C). These new F values and the second two equations are used to obtain new values for α_S and α_C . Now the new α values are input into the first two equations to obtain a modified set of F 's, and these are then input back into the second set to obtain new α 's. The process is repeated until the difference from cycle to cycle of the new values becomes negligible (In practice, this occurs very quickly, that is, in a couple of cycles). Once all unknowns are known, the evolution of the entire redox cycle is obtained as outlined at the beginning of this section.

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