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COUPLING OF THE SEDIMENTARY SULFUR AND CARBON CYCLES — AN IMPROVED MODEL

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ABSTRACT. A model of the geochemical cycles of sulfur and carbon during Phanerozoic time makes it possible to compute the masses of the major sedimentary reservoirs, their fluxes in and out of the ocean, and their isotopic compositions both forward and backward in time. The development of this model is based on an earlier study of the coupled carbon and sulfur cycles that, although conceptually correct, did not produce results reversible in time (Garrels and Lerman, 1981). The test of the validity of the new model and of the concept of coupling between the two geochemical cycles comes from results that show a reasonably good agreement between the fluctuations in size of the sulfate reservoir as predicted from sulfur isotopes and the values calculated from carbon isotopes. Large uncertainties in the estimated masses of the present-day sedimentary reservoirs (oxidized and reduced sulfur and carbon) make the conclusions of the model qualitatively useful, but they do not allow at this time a more accurate probe of the geological record for the finer causes of variation in the contents and isotopic composition of the reservoirs, such as the variations that might have been caused by changes in the global rates of continental erosion, subduction and spreading of the ocean floor, and/or additions of materials from below the crust. An important conclusion of the model, despite these caveats, is that the exogenic geochemical cycles of carbon and sulfur can be, to a reasonably good first approximation, treated as a closed system. The dominant redox system of the exogenic cycle is the complementary sulfide-sulfate–carbonate-organic carbon relation.

INTRODUCTION

The primary evidence for the coupling between the sedimentary cycles of carbon and sulfur during the Late Proterozoic and Phanerozoic, the last 700 my, comes from the isotopic records of carbon in carbonates and sulfur in sulfates of the geological column (Claypool and others, 1980; Veizer, 1983; Veizer, Holser, and Wilgus, 1980). A broad negative correlation between the $\delta^{13}C$ values of the sedimentary carbonates and the $\delta^{34}S$ values of the sulfates, along with the more detailed isotopic record of variation in $\delta^{34}S$ of the sulfates and $\delta^{13}C$ of carbonates through geological time (Claypool and others, 1980; Veizer, 1983), has been at the

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root of the attempts of several investigators (for example, Holland, 1973; Garrels and Perry, 1974; Schidlowski, Junge, and Pietrik, 1977; Claypool and others, 1980; and others) to develop mathematical models explaining the coupled behavior of the carbon and sulfur exogenic cycles. For a more recent model of Garrels and Lerman (1981), which dealt with the sedimentary cycle shown schematically in figure 1 (to be discussed in more detail later in this paper), a procedural error in computation was pointed out to the authors by Robert A. Berner in 1981. In brief, Berner's comment was directed at the computational technique we used to reconstruct the masses of oxidized and reduced carbon and sulfur backward in time, from the present to the beginning of the Phanerozoic about 600 my ago. Berner's recognition of the lack of symmetry in time of our (1981) model caused us to develop a new model for the coupled carbon and sulfur cycles that adequately represents evolution of the cycles forward in time, as from the present to the future, as well as their operation from the present to the past.

Figure 1, adapted from Garrels and Perry (1974) and Garrels and Lerman (1981), shows eight sedimentary reservoirs and an ocean and atmosphere of constant composition. The coupling between the carbon-containing and sulfur-containing reservoirs can be represented by a stoichiometric relationship accounting for transfers of materials between the reservoirs (Garrels and Perry, 1974):

$$4FeS_2 + CaCO_3 + 7CaMg(CO_3)_2 + 7SiO_2 + 15H_2O \rightleftarrows$$
$$15CH_2O + 8CaSO_4 + 2Fe_2O_3 + 7MgSiO_3 \qquad (1)$$

In the preceding reaction, discussed in detail in the two papers cited above, increase of the organic carbon reservoir (CH_2O) is at the expense of carbonate transported to the ocean from the weathering of sedimentary

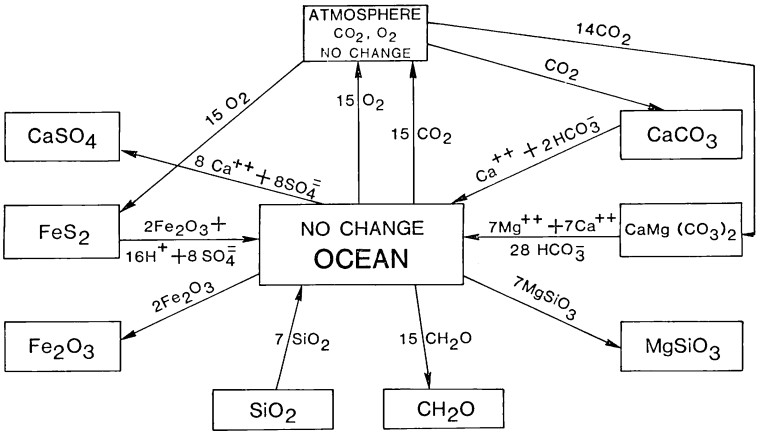

Fig. 1. Coupled changes in sedimentary reservoirs necessary to increase the gypsum ($CaSO_4$) reservoir by 8 molecular units, without changing the composition of the atmosphere-ocean system (adapted from Garrels and Perry, 1974 and Garrels and Lerman, 1981).

limestones ($CaCO_3$) and dolomites ($CaMg(CO_3)_2$). Magnesium from the dolomites ends up in sedimentary magnesium silicates (clays), whereas calcium is removed as calcium sulfate formed at the expense of the sulfur coming from oxidation of sedimentary sulfides (FeS_2). It should be noted that the above stoichiometric relationship represents *net* transfers that can take place in the sedimentary cycle. Thus, removal of 8 molecular units of $CaSO_4$ from an ocean of a constant mass and composition is accompanied by weathering of 15 molecular units of carbon from sedimentary carbonates and oxidation of 8 molecular units of sulfur from sedimentary sulfides. Because there are no calcium silicates forming in significant amounts in sediments, the coupling of reservoirs as shown in figure 1 indicates *net* transfer of calcium from the carbonate into the sulfate reservoir. Also to be noted is the production of 15 molecular units of organic matter (CH_2O), a process that produces the 15 oxygen molecules required for oxidation of 4 moles of pyrite.

The stoichiometric relationships connecting the eight sedimentary reservoirs lead to a conclusion that gains or losses in any one of them make it possible to predict the changes in the other seven. However, the complexity of the sedimentary system also makes it difficult to pinpoint the causes of transfer between the individual reservoirs: for example, excessive deposition of $CaSO_4$, resulting in an increase in the mass of the sedimentary sulfate reservoir, may be driven by a higher rate of burial of organic carbon, by an increased evaporation rate of seawater owing to the presence of extensive shallow seas, or by factors affecting any of the eight reservoirs.

The particular stoichiometric transfer equation (eq 1) was proposed by Garrels and Perry (1974), but coupling between carbon oxidation-reduction and sulfur oxidation-reduction was not a new concept in 1974 and had been proposed previously by many other scientists.

THE COUPLED CYCLE MODEL

Figure 2 represents a typical estimate of the carbon and sulfur reservoirs, $\delta^{34}S$ and $\delta^{13}C$ values, and fluxes as of "today" used in one of our calculations, where today is defined as being just prior to the time of the extensive interferences by man. The model also can be regarded as a reasonable mean situation for Phanerozoic time. The cycle model in figure 2 is at a steady state: so long as the fluxes and their isotopic values remain as shown, there will be no changes in the sedimentary reservoirs nor in the ocean-plus-atmosphere system. Such a steady state is not accurately representative of the real world at all times, but it is a useful starting point for assessing perturbations that need to be applied to achieve observed time trends of the masses and isotopic compositions of the reservoirs, still maintaining a constant mass of the ocean-atmosphere system.

Two general constraints apply to the cycle model as shown in figure 2:

1. One is the condition of a constant mass of sulfur and carbon in the ocean plus atmosphere reservoir. In the notation of figure 2, this condition requires:

$$F_{13} + F_{23} = F_{32} + F_{31} \quad (2)$$

$$F_{64} + F_{54} = F_{46} + F_{45} \quad (3)$$

The values for the masses of the ocean sulfate and carbonate reservoirs were maintained at constant values of 42×10^{18} moles S and 3.3×10^{18} moles C, respectively.

2. The second constraint is that weathering fluxes transporting materials to the ocean (fluxes F_{13}, F_{23}, F_{54}, and F_{64}) are assumed to be first-order fluxes, such that the flux is directly related to the reservoir mass, as given by

$$F_{ij} = k_{ij} M_i \qquad \text{(mass/time)} \quad (4)$$

where M_i is the mass of the reservoir, and k_{ij} is a rate parameter. In our various model calculations we used values similar to those given in figure 2 for fluxes, reservoir sizes, and δ-values of reservoirs, all of which fall within the range of values determined for these parameters by various researchers.

The sulfur cycle.—For the sulfur cycle in figure 2, we assume that the total mass of sedimentary sulfur (including the oceanic sulfate) and its mean isotopic composition remained constant during the Phanerozoic.

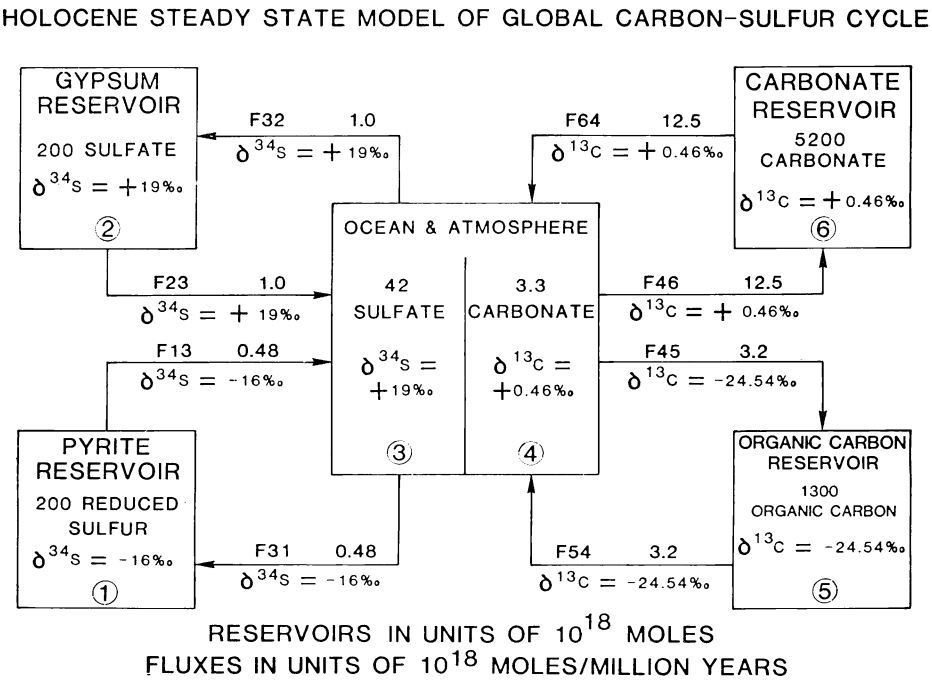

Fig. 2. A model of the coupled sulfur-carbon exogenic system. The model is in steady state with respect to masses, fluxes, and isotope values and represents an estimate of Holocene pre-man conditions, as well as a mean condition for Phanerozoic time (after Garrels and Lerman, 1981).

TABLE 1

Estimated masses of the oxidized and reduced sulfur and carbon sedimentary reservoirs (in units of 10^{18} moles). Values adjusted to the total sedimentary rock mass of 2.5×10^{24} grams

	Holser and Kaplan (1966)	Li (1972)	Garrels and Perry (1974)	Schidlowski, Junge, and Pietrik (1977)	Nielsen (1978)	Ronov and others (1980)	Garrels and Lerman (1981)	This paper
OXIDIZED S	249	147	198	196	136	158	108	200
REDUCED S	134	231	294	184	178	128	178	200
OXIDIZED C		3712	5083			7034	5200	5200
REDUCED C		930	1042	1078		1292	1300	1300

These assumptions state that the exogenic (sedimentary) cycle of sulfur is closed. Such an assumption might seem unrealistic because of the possibilities of sulfur and carbon removal by subduction of sediments or perhaps by reactions of ocean water that circulates through the hot basalts at the oceanic ridges.

However, if there were no selective removal of sulfate or sulfide from the sedimentary cycle by such mechanisms as sulfate reduction in the spreading zones, mentioned above, or subduction of sediments, then the mean isotopic composition of exogenic sulfur could be expected to be that of primordial or mantle sulfur, $\delta^{34}S = 0$ per mil. In fact, most estimates of the mean isotopic composition of sedimentary sulfur give somewhat higher values, from about +2 to +6 per mil (from the reservoir sizes in table 1), suggesting that there has been some selective removal of isotopically light sulfur from the sedimentary cycle. On the other hand, differences of mean $\delta^{34}S$ of a few per mil do not negate the proposed model.

In the 1981 and present versions of the cycle model we consider the exogenic cycle as closed throughout Phanerozoic time (total sulfur mass S_T = constant) and the mean isotopic composition of the sedimentary sulfur as representable by a fixed value ($\bar{\delta} = 0$ per mil in Garrels and Lerman (1981) and +3.2 per mil in this paper). The conditions of constant total mass and mean isotopic composition can be written in the form of the two following equations:

$$S_1 + S_2 + S_3 = S_T \tag{5}$$

$$\delta_1 S_1 + \delta_2 S_2 + \delta_3 S_3 = \bar{\delta} S_T \tag{6}$$

where subscripts refer to reservoir numbers 1, 2, and 3 (fig. 2).

If the mass of sulfur in the ocean ($S_3 = 42 \times 10^{18}$ moles) remains constant, then the changes in the masses of the sedimentary sulfates (gypsum and anhydrite, reservoir 2) and sulfide (pyrite, reservoir 1) must be of equal magnitude but opposite sign:

$$\frac{dS_2}{dt} = -\frac{dS_1}{dt} \tag{7}$$

The rate of change in the isotopic composition of sulfur in the ocean is a balance between the isotopic compositions of the input and removal fluxes, as given by the following equation:

$$\frac{d\delta_3}{dt} = \frac{1}{S_3}[\delta_1 k_{13} S_1 + \delta_2 k_{23} S_2 - \delta_3 F_{32} - (\delta_3 - \alpha_S) F_{31}] \qquad (8)$$

where $\alpha_S = 35$ per mil is the isotopic fractionation factor for biological reduction of sulfur from sulfate to sulfide.

The problem of estimating the reservoir sizes and the erosional and depositional fluxes of the oxidized and reduced sulfur through time can be stated as follows: given the geological record of variations in the $\delta^{34}S$ of sedimentary sulfates during the last 700 my (Claypool and others, 1980; fig. 3) and the three constraints of a closed cycle (eqs 2, 5, and 6), what

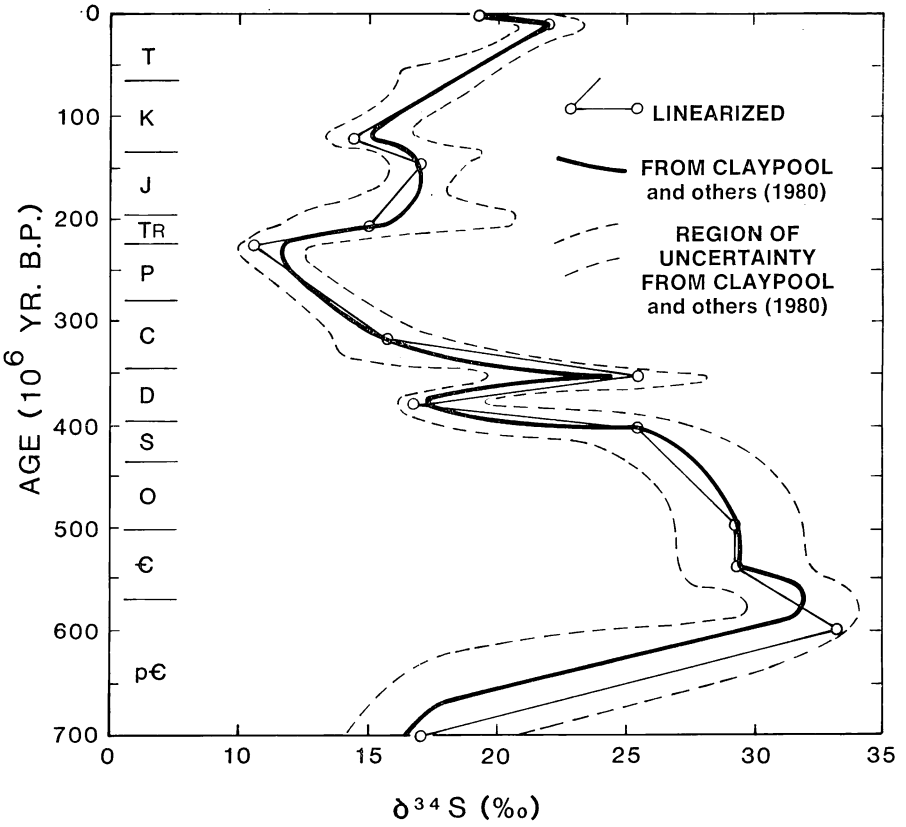

Fig. 3. The $\delta^{34}S$ values of marine $CaSO_4$ deposits over the last 700 my. The smoothed curve and the dashed lines representing the estimated error limits of values around that curve are from Claypool and others (1980). The linear segments connecting open circles are an approximation to the Claypool and others curve which was used to simplify model computations. Note that the linearization is a good approximation to the Claypool and others curve and is well within the error limits (adapted from Garrels and Lerman, 1981).

were the fluxes, the reservoir sizes of the oxidized and reduced sulfur, and their mean isotopic compositions in Late Proterozoic and Phanerozoic times? The values of $\delta^{34}S$ of the sedimentary sulfate at different times are approximately those of the ocean water from which they formed (disregarding a small fractionation of sulfur taking place during deposition of $CaSO_4$) (Holser and Kaplan, 1966). Thus, given the gradients of $\delta^{34}S$ in sedimentary sulfates in time (fig. 3) and the present-day estimates of the fluxes as shown in figure 2, eqs (8), (2), (4), (5), (6), and (7) can be solved to obtain future values of F_{13}, F_{23}, δ_1, δ_2, S_1, and S_2 over the time interval for which a change in δ_3 holds for the ocean.

The rate of change in the mass of the sedimentary sulfate reservoir (S_2) in the future is a balance between the depositional (F_{32}) and erosional (F_{23}) fluxes,

$$\frac{dS_2}{dt} = F_{32} - k_{23}S_2 \tag{9}$$

where the erosional first-order flux F_{23} is written in the notation of eq (4).

The rate of change in the mean isotopic composition of gypsum, reservoir 2, is obtained by differentiation of δ_2 in (6):

$$\frac{d\delta_2}{dt} = \frac{1}{S_2}\left[-\delta_2 \frac{dS_2}{dt} - \frac{d(\delta_1 S_1)}{dt} - \frac{S_3 d\delta_3}{dt}\right] \tag{10}$$

The numerical solution method solves a system of simultaneous differential equations, such as (7)-(10), over geologically short time steps, 10^5 yr or shorter, for segments of time of 10^7 to 10^8 yr, during which the trends in $\delta^{34}S$ of ocean water (fig. 3) persist. The results are the values of the reservoir sizes, their mean isotopic compositions, and the erosional and depositional fluxes as functions of time.

The carbon cycle.—The mathematical form of the carbon cycle can be made considerably simpler than that of the sulfur cycle. First, the stoichiometric eq (1) for transfers among the sedimentary reservoirs indicates that the mass of organic carbon stored over a short period of time (ΔC_5) is related by a factor 15/8 to the change in the mass of sulfur in the $CaSO_4$ reservoir:

$$\Delta C_5 = +\frac{15}{8} \cdot \frac{dS_2}{dt} \cdot \Delta t \tag{11}$$

Second, the flux of carbon into or out of the oceans each million years is about 5 times the total carbon content of the ocean and atmosphere. Therefore, on the time scales with which we are dealing, it can be assumed that a change of the fluxes into or out of the ocean produces an instantaneous response, and that the carbon in the ocean and atmosphere can be neglected in considering the effects of flux changes. (This assumption is borne out by detailed calculations.) Because of this simplification, it follows that the mean isotopic composition of the inputs to the ocean must be the same as the mean isotopic composition of the outputs, leading to the relationship:

$$\bar{\delta}(k_{54}C_5 + k_{64}C_6) = \delta_4 F_{46} + (\delta_4 - \alpha_C)F_{45} \quad (12)$$

where, as in figure 2, C_5 is the mass of the organic carbon reservoir, C_6 is the mass of the limestone reservoir, and α_C is the isotopic fractionation factor for biological reduction of carbon (we take $\alpha_C = 25$ per mil). The mean isotopic composition of the inputs to the ocean ($\bar{\delta}$) can be taken as a constant because the rate parameters for erosion of the two carbon reservoirs are nearly equal, $k_{54} \cong k_{64}$.

By an iterative computation, the values of F_{45} can be evaluated from the computed changes in masses of the $CaSO_4$ reservoir (eq 11), giving the new reservoir masses C_5 and C_6, from which the depositional fluxes F_{45} and F_{46} can be computed.

EARLIER AND NEW MODELS

In our initial model (Garrels and Lerman, 1981), we reasoned as follows: If we wish to create the sulfur reservoirs and their $\delta^{34}S$ values in Miocene time, 12 my ago, we can use the $\delta^{34}S$ value of Miocene sulfate deposits (+22 per mil), as compared to our Holocene value in figure 2 (+19 per mil), to recreate Miocene conditions. To do this we will run *forward in time*, using the mathematical relation developed above, from present day conditions, adjusting fluxes and reservoirs, until an oceanic (and hence contemporary gypsum deposit) $\delta^{34}S$ of +22 per mil is achieved. We then assume that the reservoir sizes and $\delta^{34}S$ values of the reservoirs of sulfate and sulfide are indeed those of Miocene time, and that if these Miocene values were used to reverse the calculation to go *forward in time again* to the present day $\delta^{34}S$ value of +19 per mil, we would have reproduced the real process of going forward in time from the Miocene to the Present. Figure 4 shows schematically the argument used, that legs A → B and C → D should be identical, and that the reservoir sizes and isotope ratios at the end of leg C → D should be the same as those at the beginning of leg B → C.

Using our original model and running 12 my into the future, adjusting the fluxes of sulfate and sulfide from the oceans to achieve a $\delta^{34}S$ of the ocean of +22 per mil, produces the values for the masses of the sulfate and sulfide reservoirs, and their mean $\delta^{34}S$ contents shown at the end of leg B → C. If these numbers, and the same rate constants, are used to go 12 more million years into the future, adjusting the sulfate and sulfide fluxes out of the oceans so as to return the $\delta^{34}S$ of the oceans to +19 per mil, the resulting values are those shown in the box at D. Clearly, operating the model by running it forward for a selected time span to achieve a given value of $\delta^{34}S$ for the ocean, and then continuing forward in time for an equal time span, adjusting the fluxes out of the ocean so as to return to the initial $\delta^{34}S$ ocean value, does not produce symmetrical and reversible results.

This incorrect feature of the model was pointed out to us by Robert Berner of Yale University. Berner (personal commun., 1981) used the model of Garrels and Lerman (1981) to produce results for a given period of time into the future in such a manner as to achieve a desired $\delta^{34}S$, just

as shown for the leg B → C in figure 4. However, he adjusted the reservoir sizes at time point C so that a return to the original $\delta^{34}S$ of the ocean (leg C → D) reproduced the starting reservoir sizes and $\delta^{34}S$ values. Berner thus used a classic technique of assuming conditions in the past and showing that running the model to the present can produce present-day conditions, pointing out that the computed path C → D is the same as the path A → B, a feature that was in error in our 1981 model. This method was then continued by "stepping-back" further in time in small steps and running the program forward so as to arrive at already calculated points (for example, point C in our example, fig. 4).

Despite the error in our 1981 model, it will be shown in the next section that the major aspect of the model — the coupling between the

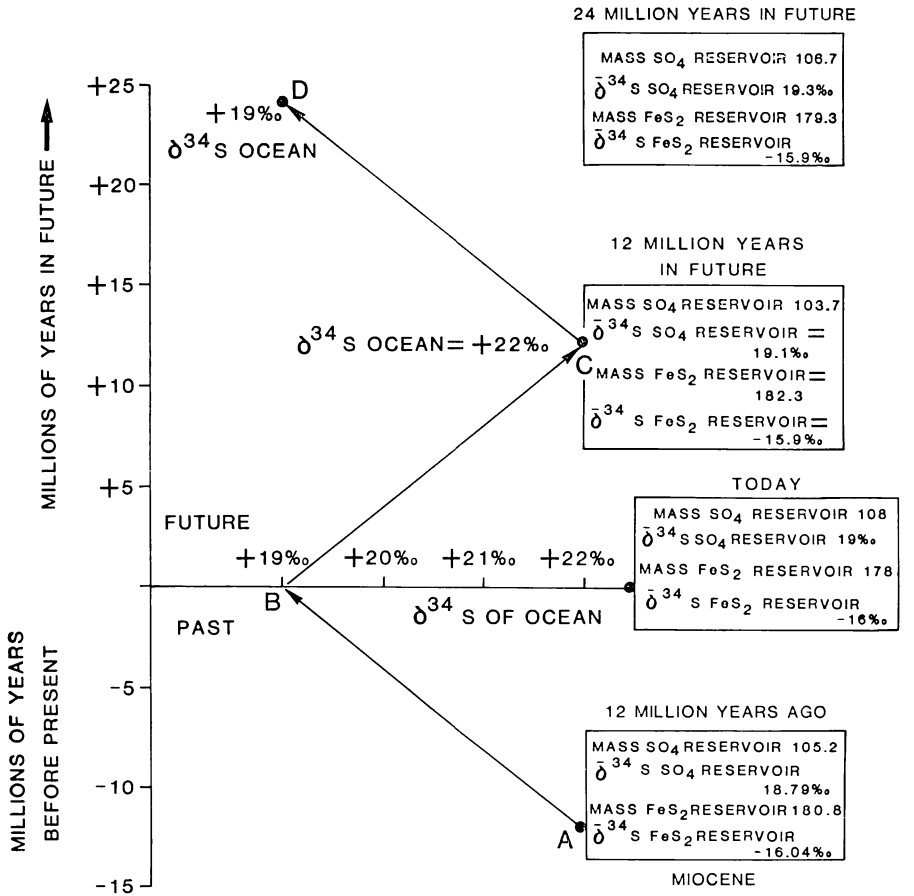

Fig. 4. Diagram showing that calculation of the masses and $\delta^{34}S$ values of sulfur reservoirs from an initial $\delta^{34}S$ of the ocean to a new value in the future, over a given time period, followed by a return to the initial $\delta^{34}S$ of the ocean over another equal time period, is not a symmetrical process. The numerical values in the boxes show the extent of the asymmetry involved in the Garrels and Lerman article of 1981.

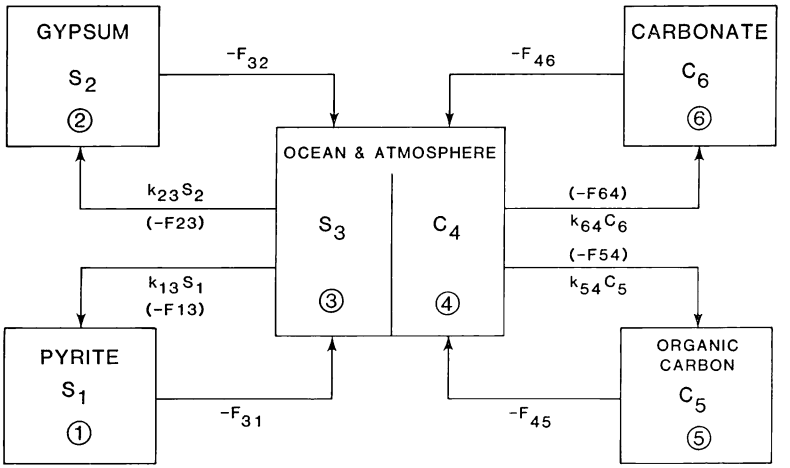

Fig. 5. The reversals of fluxes, as compared with the model presented in figure 2, required to run the carbon-sulfur model backward in time.

carbon and sulfur reservoirs — was not violated, as borne out by the comparison of our old, Berner's, and the new results.

THE "MOVIE MODEL" — REVERSIBILITY IN TIME

To make a model of the coupled carbon and sulfur cycles correctly reversible in time, the model must, starting with some assumed values of the reservoir sizes and their isotopic compositions at some point in time, produce values into the future and — most significantly — starting with the derived future values, it must, if run backward, reconstruct the original assumed conditions.

We realized that reversing time in our model must have the basic attributes of running a movie film backward — divers rise out of the water and return to the springboard; the water displaced by the diver's entry into the water returns through the air to fill the hole the diver originally produced; and so on.

Therefore, to go backward in time from a given set of conditions, we constructed a model of a reversed cycle, in which the rivers run out of the ocean, returning the sulfate and carbonate that had been eroded to their sources. In the time-backward model, gypsum dissolves into the ocean instead of precipitating from it, and pyrite is formed in its reservoir by giving oxygen back to the atmosphere; it is removed from its reservoir by returning to the ocean. In essence all the relationships between the reservoirs and fluxes as shown in figure 2 are retained in the movie model, except that the algebraic signs of the fluxes become reversed. Schematically, the movie model is shown in figure 5, where the reversed directions of the fluxes should be noted. The rate of mass change in the gypsum reservoir, compare eq (9), is in the movie model

$$\frac{dS_2}{dt} = -F_{32} + k_{23}S_2 \qquad (13)$$

and the rate of change in the isotopic composition of oceanic sulfate, eq (8), is

$$\frac{d\delta_3}{dt} = \frac{1}{S_3}[-\delta_1 k_{13} S_1 - \delta_2 k_{23} S_2 + \delta_3 F_{32} + (\delta_3 - \alpha_S) F_{31}] \qquad (14)$$

It is important to emphasize that the "backward-run-movie-model" gives the conditions of yesterday from the known conditions of today, from the known length of time between yesterday and today, and, above all, from the "known" mathematical model that describes the changes taking place from yesterday to today. For example, if either eq (9) or (13), representing the change in the $CaSO_4$ reservoir mass with time could be solved explicitly by straight-forward integration, then either a later value, S_2 at t_1, or an earlier value, S_2 at t_0, could be computed explicitly if either one of the two were known. Our model, however, is based on a numerical solution of a system of simultaneous differential equations, where computation of yesterday's conditions from those of today is not as simple nor obvious as in a case of one reservoir.

Results.—Results of a test of the model over a 12 my time span are shown in table 2. The effects of a change from oceanic $\delta^{34}SO_4$ of +19 per mil today to +22 per mil have been calculated. Then the fluxes were reversed, and the system was reevaluated as of today. Clearly, the model produces data that are reversible in time within the limits of the rounding-off errors.

Once the validity of the techniques for time reversal was established, a variety of calculations representing conditions of the Phanerozoic were collected.

TABLE 2

Results of computation of the sedimentary sulfate (gypsum) reservoir size and its mean isotopic composition. Values at time 0 taken from Garrels and Lerman (1981). Computed values from 0 to 12 my forward in time are essentially the same as those obtained by a "reversed time" model, computing backward in time, from 12 my to 0

	Sulfate reservoir mass (10^{18} moles S)		Mean $\delta^{34}S$ of sulfate reservoir (‰)	
Time (10^6 yr)	Forward in time (0-12)	Backward in time (12-0)	Forward in time (0-12)	Backward in time (12-0)
0	108.0	108.0	19.000	19.004
1	107.70	107.69	19.001	19.005
2	107.39	107.38	19.003	19.007
3	107.06	107.05	19.007	19.011
4	106.72	106.71	19.012	19.016
5	106.38	106.37	19.019	19.023
6	106.02	106.01	19.027	19.030
7	105.65	105.64	19.036	19.040
8	105.28	105.27	19.047	19.050
9	104.89	104.89	19.059	19.061
10	104.49	104.48	19.071	19.074
11	104.09	104.08	19.085	19.087
12	103.67	103.67	19.100	19.100

Sulfate and sulfide reservoir sizes.—There is a wide variation among the estimates of the sizes of the sedimentary sulfur and carbon reservoirs as reported by different investigators. For the reduced and oxidized sulfur reservoirs, estimates vary by as much as a factor of two. Some of the estimates from the literature are summarized in table 1, along with the values used in this paper. The masses of the sulfate and sulfide reservoirs, taken as equal at 200×10^{18} moles, differ from the estimates used in the earlier version of the cycle model (Garrels and Lerman, 1981), but they fall within the range of the individually reported values. Whichever values are used in the model, large uncertainties are associated with them because of inadequate data on the sedimentary reservoirs.

Movie model calculations.—Table 3 gives calculated values for the characteristics of the sulfur sedimentary system for the past 700 my, using the revised backward-forward time model with the parameters given in the caption. The forcing function is the sulfur isotope curve of Claypool and others (1980), shown in figure 3 and in the δ_3 values in the table.

Comparison of existing models.—Figure 6 is a compilation of the calculated sizes of the sulfate reservoir as a function of time over the last 700 my. The curves, as explained in detail in the caption, are based on a variety of assumptions concerning initial reservoir sizes and flux rates. Some of the curves are generated from the Present backward in time, others assume conditions for the past and are calculated to the Present. The values found by Schidlowski, Junge, and Pietrik (1977) and by

TABLE 3

Sulfur cycle. Results of a "backward movie run" from the Present to the Late Proterozoic. Ocean water values of the isotopic composition of sulfur in sulfate (δ_3) are from figure 3. Erosion rate constants $k_{13} = 0.0025$ and $k_{23} = 0.0050$ per 10^6 yrs. Mean $\delta^{34}S = 3.17$ per mil, $\alpha = 35$ per mil

Time BP (10^6 yr)	δ_1	δ_2	δ_3	S_2	S_1	F_{32}	F_{31}
		‰		10^{18} moles S		10^{18} moles S/10^6 yr	
0	−15.04	18.09	20.00	198.5	201.5	0.96	0.54
22	−15.35	17.76	21.36	200.7	199.3	0.90	0.60
42	−15.07	17.48	20.09	202.3	197.7	0.96	0.54
82	−14.24	17.17	17.55	202.4	197.6	1.07	0.44
122	−13.18	17.39	15.00	197.7	202.3	1.18	0.31
160	−13.00	17.61	16.57	193.0	207.0	1.09	0.39
200	−12.17	18.04	15.32	186.3	213.7	1.14	0.33
220	−11.33	18.54	12.50	181.2	218.8	1.25	0.19
250	−11.12	19.83	13.53	170.8	229.2	1.20	0.23
280	−10.91	21.19	14.56	160.7	239.3	1.14	0.26
310	−10.69	22.66	15.59	150.8	249.2	1.08	0.30
350	−11.37	24.18	22.50	140.9	259.1	0.78	0.57
400	−11.38	25.32	25.10	133.6	266.4	0.66	0.67
460	−12.21	24.99	27.86	137.6	262.4	0.56	0.78
500	−13.24	24.40	29.70	144.9	255.1	0.49	0.87
540	−14.30	23.65	29.60	155.0	245.0	0.51	0.88
580	−16.11	22.80	31.20	168.1	231.9	0.45	0.97
620	−18.03	21.87	29.60	184.9	215.1	0.54	0.92
660	−18.62	21.10	24.80	196.7	203.3	0.78	0.71
700	−18.22	20.85	20.00	201.1	198.9	1.00	0.50

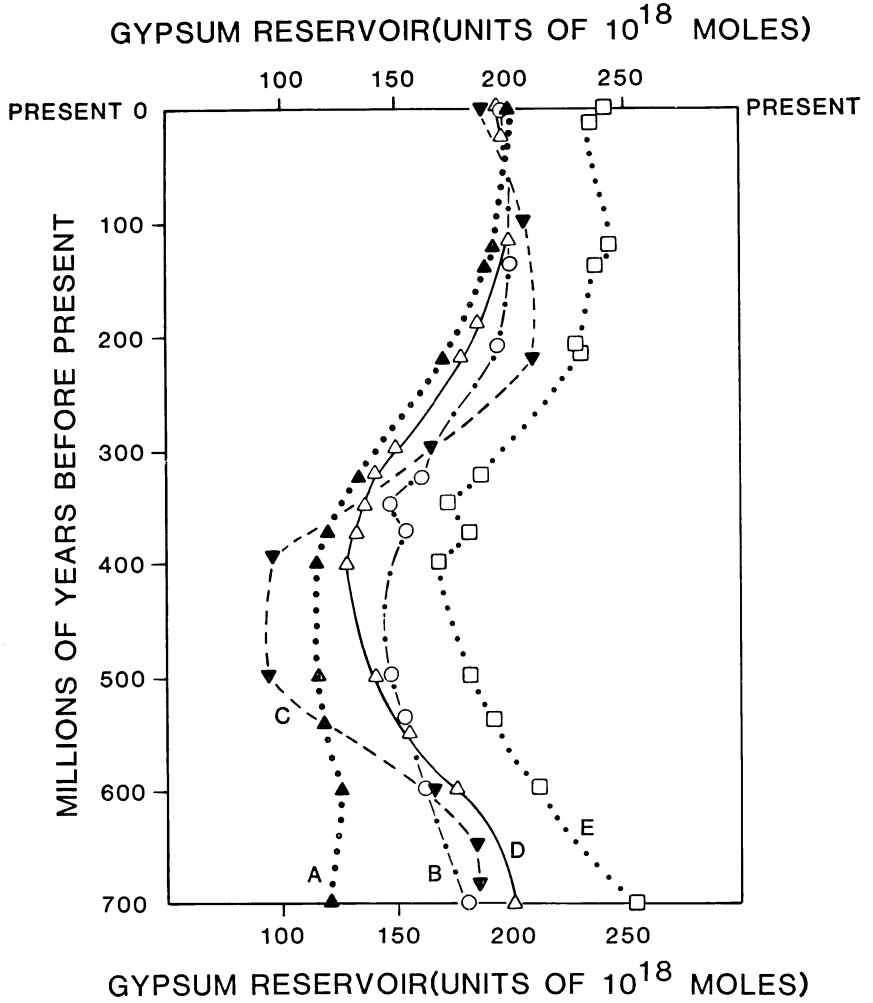

Fig. 6. Comparison of calculated sizes of the $CaSO_4$ reservoir as a function of time by various investigators. All calculations assume a constant fractionation of 35 per mil between sulfate and sulfide and constant (but not equal) total sulfur in the model, as well as a constant and equal sulfate in the ocean equal to 42 × 10^{18} moles. The other parameters used are given below.

A. ▲ • • • ▲ (this paper) Initial present-day reservoirs: sulfate = sulfide = 200 × 10^{18} moles; $\delta^{34}S$ values: ocean = +20 per mil, gypsum = +18.5 per mil, sulfide = −15.7 per mil; erosion rate constants: K_{13} = 0.0025, K_{23} = 0.0050; older values calculated from present backward by "movie technique" from linearized, observed values for $\delta^{34}S$ on the curve of Claypool and others (1980).

B. ○ — • — • — ○ (Berner, personal commun., 1981) Initial present-day reservoirs: sulfate = sulfide = 200 × 10^{18} moles; $\delta^{34}S$ values: ocean = +19 per mil, gypsum = +19 per mil, sulfide = −16 per mil; erosion rate constants: K_{13} = 0.0020, K_{23} = 0.0040; older values calculated from present by step-back technique (see text).

C. ▼ — — — ▼ (Schidlowski and Junge, 1981) Based on a budgeting technique beginning with conditions 1000 × 10^6 yrs ago. Values taken from their summary graph of deduced relations.

D. △———△ (this paper) Reservoir sizes 700 × 10^6 yrs ago: sulfate = sulfide = 200 × 10^{18} moles; $\delta^{34}S$ values (700 my BP): ocean = +17 per mil (from Claypool and others, 1980), gypsum = +19 per mil, sulfide = −16 per mil; erosion rate constants: K_{13} = 0.0025, K_{23} = 0.0050; present values calculated from 700 × 10^6 yrs ago to the present.

E. □ • • • □ (Berner, personal commun., 1981) Reservoir sizes 700 × 10^6 yrs ago: sulfate = sulfide = 255 × 10^{18} moles; $\delta^{34}S$ values (700 my BP): ocean = +17 per mil, gypsum = +19 per mil, sulfide = −16 per mil; erosion rate constants: K_{13} = 0.0020, K_{23} = 0.0040; present values calculated from 700 × 10^6 yrs ago to the present.

Schidlowski and Junge (1981) are derived from a "budget model," rather than a box model; the reader is referred to the original articles for details of their modeling. However, all the calculations shown are for closed systems, and the Schidlowski-Junge model includes a sediment cycling term that is roughly equivalent to the rate constants used in the box models.

The trends deduced by the various modelers are similar. The sulfate reservoir decreased from 700 to 400 my ago, then increased strikingly, reaching a maximum between 220 and 100 my ago. Since then it has declined slightly. The range of mass is about 80×10^{18} moles in all the models. This range corresponds to a change in the organic carbon reservoir (oxygen production) of 150×10^{18} moles, about 4 times the oxygen in the present atmosphere.

TABLE 4

Coupled carbon and sulfur cycles. Isotopic composition of carbon in limestones in ocean water (δ_4) from Veizer (1983). The mass of the organic carbon reservoir (C_5) and depositional fluxes to the organic carbon (F_{45}) and oxidized carbon (F_{46}) reservoirs computed as explained in the text, using the following parameter values: erosional rate constants for the two carbon reservoirs $k_{54} = k_{64} = 0.0019$ per 10^6 yrs, fractionation factor for biogenic reduction of carbon $\alpha_C = 25$ per mil, and mean isotopic composition of carbon in inflow to the ocean $\bar{\delta} = -3.73$ per mil. The mass of the oxidized sulfur reservoir (S_2) computed from the masses of the reduced carbon (C_5) shown in the table. See figure 7

Time BP (10^6 yr)	δ_4 ‰	C_5	S_2	F_{45}	F_{46}
		10^{18} moles C or S		10^{18} moles C/10^6 yrs	
0	0.5	1300	200	2.09	10.26
12	1.6	1302	201	2.66	9.69
28	1.1	1301	201	2.41	9.94
48	1.5	1301	200	2.61	9.74
56	2.2	1298	199	2.96	9.39
60	1.3	1297	199	2.51	9.84
68	1.9	1296	198	2.81	9.54
96	2.2	1284	192	2.96	9.39
108	2.7	1277	188	3.21	9.14
136	0.4	1272	185	2.06	10.29
164	2.4	1268	183	3.06	9.29
220	0.3	1262	180	2.01	10.34
232	2.8	1259	178	3.26	9.09
272	3.4	1218	156	3.56	8.79
280	2.3	1210	152	3.01	9.34
292	4.0	1197	145	3.86	8.49
340	0.4	1163	127	2.06	10.29
352	1.6	1161	126	2.66	9.69
360	0.1	1161	126	1.91	10.44
372	0.9	1162	127	2.31	10.04
408	−0.2	1170	130	1.76	10.59
420	1.9	1169	130	2.81	9.54
452	−0.2	1168	129	1.76	10.59
488	−1.1	1194	143	1.31	11.04
496	0.0	1199	146	1.86	10.49
508	−0.7	1207	150	1.51	10.84
564	−0.9	1257	177	1.41	10.94
700	1.0	1342	223	2.36	9.99

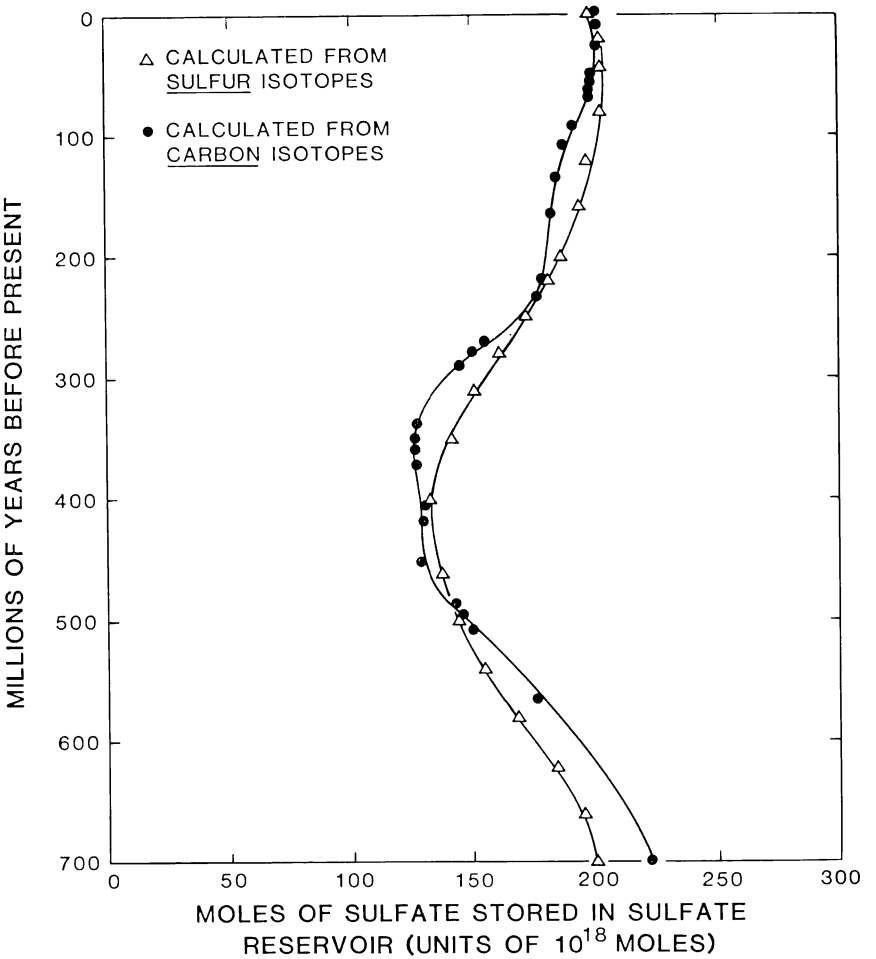

Fig. 7. Diagram showing calculated variations of sulfate storage in the sulfate (gypsum) reservoir for the last 700 my. The curve designated by open triangles (△) was calculated from the sulfur isotope data (Claypool and others, 1980), and the curve designated by closed circles (●) was calculated from the carbon isotope data (Veizer, 1983). The data are taken from tables 3 and 4, respectively.

Many more calculations are required to determine the "sensitivity" of the models to changes in their basic parameters. The two curves by Berner (B and E) in which he changed only the amount of total S of the system, indicate that *changes* of sulfate storage are about the same, even if total sulfur estimates are quite different. Our own work (A and D) indicates a considerable sensitivity to the mean values of $\delta^{34}S$ chosen for the sulfate and sulfide reservoirs of the basic steady-state model, used as an initial condition. We have discovered a similar sensitivity to the mean values chosen for the carbonate and carbon reservoirs. Note that our "movie model" uses initial mean $\delta^{34}S$ values for the reservoirs somewhat

different from the models of Berner and also slightly different from the values of figure 2.

CARBON AND SULFUR RESERVOIRS FROM $\delta^{13}C$ CURVE

The coupling between the carbon and sulfur cycles is represented by eq (11). Thus, using the computed values of the sedimentary sulfate reservoir (S_2) through time, as shown in figure 6, one can estimate the carbon reservoir sizes and the fluxes in the carbon system. An alternative approach that we adopted was to use a new set of $\delta^{13}C$ data for the Phanerozoic limestones, prepared by Veizer (1983), and to compute from these data the carbon reservoir masses, the fluxes between them and, finally, the sulfate reservoir mass varying through time. The results of these computations are shown in table 4 and figure 7. The $CaSO_4$ reservoir mass, computed from the carbon-cycle results, varies in a manner similar to the $CaSO_4$ mass computed from the sulfur-isotope data. The maximum difference between the two curves for S_2 against time is about 25×10^{18} moles S, well within the variation between the individual estimates of the $CaSO_4$ reservoir sizes given in table 1. However, this difference between the results of the two methods is equivalent to about 50×10^{18} moles O_2 stored in the sedimentary sulfates, an amount about 30 percent greater than the mass of oxygen in the present-day atmosphere.

The depositional flux of reduced carbon (F_{45}) in this model was computed from eq (12):

$$F_{45} = \frac{1}{\alpha_C}(\delta_4 - \bar{\delta})F_T \tag{15}$$

where α_C is the isotopic fractionation factor for biogenic reduction of carbon in ocean water, $F_T = F_{45} + F_{46}$ is the total carbon flux either into or out of the ocean, as defined in eq (3), δ_4 is the $\delta^{13}C$ value in limestones (Veizer, 1983) that we equate with the ocean water value, and $\bar{\delta}$ is the mean isotopic composition of carbon in inflow to the ocean, essentially identical to the mean $\delta^{13}C$ of the sedimentary carbon (that is, the mean of limestones, organic carbon, and ocean plus atmosphere reservoirs). We took the value of mean isotopic composition at $\bar{\delta} = -3.73$ per mil that is compatible with the reservoir sizes and fractionation factor used in this paper ($C_5 = 1300 \times 10^{18}$, $C_6 = 5200 \times 10^{18}$ moles C, $\alpha_C = 25$ per mil), and with the mean value of $\delta^{13}C$ for the Phanerozoic $CaCO_3$ reservoir lying between 1.2 and 1.3 per mil, as shown by the $\delta^{13}C$ curve of Veizer (1983). The value of the total flux of carbon (F_T) was taken as

$$F_T = k_{54}(C_5 + C_6) = 0.0019 \times 6500 \times 10^{18} = 12.35 \times 10^{18} \text{ moles C}/10^6 \text{ yrs.}$$

The $\delta^{13}C$ against time curve (Veizer, 1983) shows numerous changes in its slope. At the points where change in slope occurs (that is, where $d\delta_4/dt = 0$), the steady-state depositional flux F_{45} was evaluated using eq (15). Between any two points in time for which the fluxes were determined, we assumed that the flux changes linearly. Thus, the rate of change in the mass of the reduced carbon reservoir (dC_5/dt) can be

related to the variable depositional flux $F_{45}(t)$ and the reservoir erosion, as follows:

$$\frac{dC_5}{dt} = F_{45}(t) - k_{54}C_5 \tag{16}$$

Between any two points in time, such as those listed in table 4, eq (16) can be solved explicitly, when the rate parameter $k_{54} = 0.0019$ per 10^6 yr is constant, and the depositional flux varies linearly, in a form $F_{45}(t) = F_0(1 + bt)$. The masses of the reduced carbon reservoir (C_5) computed in this fashion are listed in table 4. The mass of the $CaCO_3$ reservoir, not listed in the table, is a complement of 6500×10^{18} moles C, or $6500 \times 10^{18} - C_5$. The computation was carried out backward in time, from the present-day values $C_5 = 1300 \times 10^{18}$ moles C and $S_2 = 200 \times 10^{18}$ moles S. The gypsum reservoir mass was computed using eq (11) and the values of C_5 listed in table 4.

CONCLUSIONS

A reasonably good agreement between the fluctuations in size of the sulfate reservoir, as predicted from sulfur isotopes, and the values calculated from carbon isotopes, shows that reduction of carbonate carbon to organic carbon is, indeed, mirrored in a roughly comparable oxidation of reduced sulfur to oxidized sulfur over time periods of tens of millions of years (fig. 7). This relationship is a consequence of a remarkable coupling among the sedimentary reservoirs in a world that cannot afford wild fluctuations in the oxygen and carbon dioxide contents of the atmosphere without eliminating life. In the ultimate analysis of the chemical and mass changes in the sedimentary reservoirs taking place over time segments of tens of millions of years, it can be observed that permissible changes in the atmospheric and oceanic reservoirs of carbon, sulfur, calcium, magnesium, and other compounds or elements are so small relative to transfers of materials among the sedimentary reservoirs, that the ocean plus atmosphere system must be regarded as a medium of transfer, but not a medium of storage.

Even though the relationships between the sulfur and carbon cycles as presented in this paper are not well constrained quantitatively (note the wide error limits on fig. 3), the fact that they are qualitatively significant leads to important consequences. For example, variations in the flux of organic carbon to sediments during the last 700 my need not be more than about 50 percent greater or less than the average values to explain the observed $\delta^{34}S$ of sulfates and $\delta^{13}C$ of carbonates during the same time span. This conclusion may significantly support the idea that the world 700 my ago was not markedly different from the world of today in terms of rates of erosion and deposition. This general conclusion may not seem important, but one of the major problems in recreating ancient environments is the absence of restraints on previous physical conditions.

Another important conclusion from the results of the cycle model is that a model treating the exogenic cycle as a closed system produces

results that are qualitatively valid. Further demonstration of the validity of a closed model is the agreement between model-predicted and measured changes in the rates of *sedimentary* pyrite sulfur burial over Phanerozoic time, as shown recently by Berner and Raiswell (1983). This conclusion has far-reaching implications: it indicates that a closed exogenic system is, to a first degree, a valid model of the surface environment of the Earth. In this case, the effects of removals and additions to the system by such processes as ocean-floor spreading, subduction of the crust down Benioff zones, hot springs, volcanism, and similar processes on a large scale, do not upset a closed-system exogenic model. None of the global removal or addition processes is negated by the cycle model, but there is a strong implication that all of these processes contribute to the return of the volatiles — especially CO_2 and S — to the exogenic system — one of the requirements for treating the exogenic cycle as a closed system.

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