

Phanerozoic cycles of sedimentary carbon and sulfur

(isotopes/sediment cycles/natural oxygen reservoirs)

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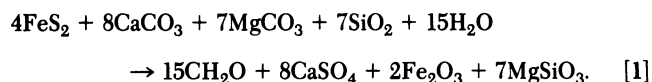
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ABSTRACT A reservoir model of a Recent steady-state sedimentary system in which the reduced sulfur and oxidized sulfur reservoirs were coupled with the oxidized carbon and reduced carbon reservoirs was constructed. The time curve of the sulfur isotope ratios of the sedimentary sulfate reservoir was used to drive the model back to the beginning of Cambrian time (600 million years ago), producing the reservoir sizes and isotope values and material fluxes of the carbon-sulfur system. The predicted values of carbon isotope ratios of the carbonate reservoir agree well with observed values, showing that the model is basically sound. Some general conclusions from this success are (i) material flux rates in the carbon-oxygen-sulfur system of the geologic past (averaged over tens of millions of years) lie within about a factor of 2 of Recent rates. (ii) The oxidation-reduction balances of Phanerozoic time were dominated by reciprocal relationships between carbon and sulfur compounds. (iii) The rate of production of atmospheric oxygen by storage in sediments of organic carbon of photosynthetic origin increased from the Cambrian Period to the Permian Period and declined somewhat from the Permian Period to the Present. (iv) The storage of oxygen in oxidized sulfur compounds kept pace (within the limits of the data) with oxygen production. (v) Transfer of oxygen from CO₂ to SO₄ from the Cambrian to the Permian Period was several times the Recent free oxygen content of the atmosphere.

In recent years attempts have been made to interpret the biogeochemical processes in the Earth's surface environment within a framework of *cycles*. A conceptual model of a cycle of one or more elements is generally a system of reservoirs representing different compartments of the environment and fluxes transporting materials among them.

Most criteria that might be used to indicate secular trends of the sizes of sedimentary reservoirs or fluxes of the global sedimentary system indicate that reservoir sizes and fluxes change with time, but that there are no pronounced trends. One might liken the reservoir system changes to those of the water content of a number of aquaria, linked by pipes, that would take place if the aquaria were mounted in the hold of a ship. Water would move among the reservoirs as the ship pitched and rolled, but one could conceive of a "mean steady state," the contents of the reservoirs at the mean position of the ship. We visualize the reservoirs of sedimentary materials during the last half-billion years as conforming to such a model—some reservoirs changing their masses by factors of two or three, perhaps, but with no change in the total mass of all reservoirs or in the ocean-atmosphere system that is the medium of transfer, and a general oscillation of mass of a given reservoir around a mean value. Fig. 1 shows the stoichiometry required for increase of mass of the CaSO₄ reservoir. The transfer involves 10 reservoirs: atmosphere, ocean, and eight reservoirs of mineral phases and organic matter. The arrows between the reservoirs indicate

material transport, such as gas exchange, deposition from the ocean, and dissolution and weathering of rocks that produce inputs to the ocean. Despite the variety of reservoirs and fluxes in Fig. 1, this model depicts the biogeochemical cycles of only three main elements—carbon, sulfur, and oxygen—and the ancillary roles of several other elements (Fe, Mg, Ca, Si), through which the C, S, and O reservoirs and fluxes are connected to one another. The individual transfers between the reservoirs in Fig. 1 can be represented by a net balance equation for the transfer fluxes (1) written in the form of a stoichiometrically balanced chemical reaction:



The process of accumulating 8 (8 is arbitrary and for illustrative purposes) molar units of Ca and SO₄ in gypsum or anhydrite can be followed descriptively as follows. The sulfur stored in SO₄ must come from oxidation of reduced sulfur from the FeS₂ reservoir, which requires 15 O₂ and produces 2 Fe₂O₃ and 16 H⁺ along with the required 8 SO₄²⁻. The replacement of 15 O₂ consumed from the atmosphere is accounted for in part (8 O₂) by photosynthesis of 8 CO₂ released from the CaCO₃ reservoir by storage of 8 Ca²⁺ in gypsum. Production of 8 O₂ from 8 CO₂ also requires burial of 8 C in organic carbon. The other 7 O₂ required for SO₄²⁻ must come from photosynthesis of CO₂ yielded by the MgCO₃ component of carbonate rocks (shown as the MgCO₃ reservoir in Fig. 1). The 7 O₂ are released by transfer of Mg from carbonate to silicate, that is, from dolomite to clay. This CO₂ cannot be derived from CaCO₃ conversion to CaSiO₃ because Ca is stored in large quantities in sediments only as carbonate or sulfate. Calcium silicates do not form in the surface environment. The carbon of the MgCO₃-derived CO₂ is stored as organic C.

The preceding brief description of the cycle seems to indicate that gypsum deposition may be the driving force of the system. Conversely, Eq. 1 also results from the assumption of accumulation of organic carbon without change in the composition of ocean or atmosphere. Briefly, storage of 15 CH₂O requires 15 C from carbonates and produces 15 O₂ in the ocean plus atmosphere. The sink for the free O₂ is oxidation of reduced sulfur and iron.

CARBON-SULFUR MODEL

Essential data and constraints of the model

The system of Fig. 1 can be used as the basis for a mathematical model of the carbon-sulfur cycle. Starting with the modern, but prehuman, carbon-sulfur system, the system is driven back-

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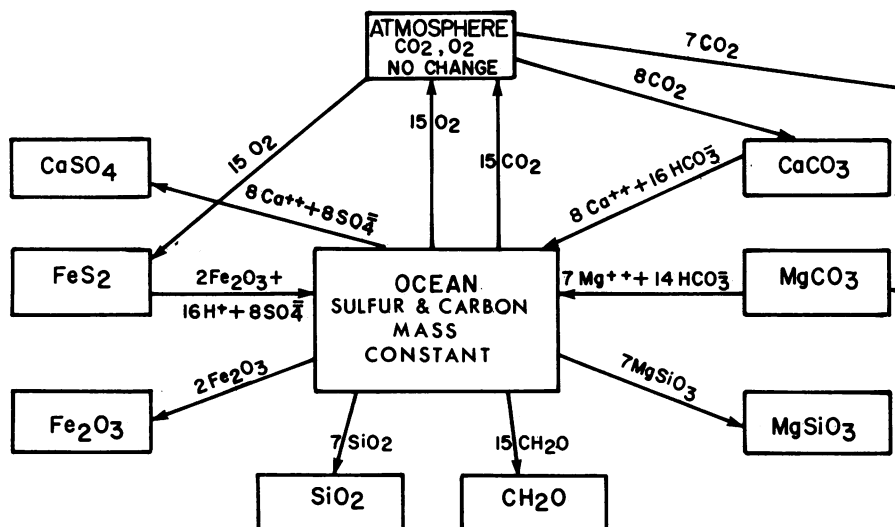


FIG. 1. Main sedimentary reservoirs and transfers in a system of constant ocean and atmosphere, corresponding to Eq. 1. An increase in the CaSO₄ reservoir by 8 molar units corresponds to an increase in the organic carbon reservoir (CH₂O) by 15 molar units.

ward through time so as to simulate the observed distribution of sulfur isotopes in evaporites. The values of the carbon isotopes in carbonates are derived from the model and compared to the observed values.

A number of models related to the cycles of reduced and oxidized carbon and sulfur and their reservoirs and fluxes have been developed during the last decade (1-5).

Fig. 2 shows the model used for our computation. It represents the world just prior to man's interference.

The model of the cycles in Fig. 2 is balanced. That is, as long as the cycles remain unperturbed, there would be no changes in reservoir contents and fluxes as functions of time, and there would have been no change in the numbers shown in the figure. The masses of the sulfur and carbon reservoirs and of the individual mass fluxes were derived from several sources (6-9) and made internally consistent. For example, the molar ratio of organic carbon to reduced sulfur in marine sediments has been established at 0.14 (10). The value from our model in Fig. 2 is: $F_{31}/F_{45} = 0.48/3.2 = 0.15$.

The following brief points should be mentioned with regard to the isotopic δ values of S and C in the individual reservoirs and fluxes of Fig. 2. (i) The mass of the ocean plus atmosphere reservoir of sulfur (dissolved sulfate) and carbon (largely dissolved bicarbonate and atmospheric CO₂) is assumed constant through time. (ii) The mean $\delta^{34}\text{S}$ value of sulfur (gypsum plus pyrite plus ocean) is the primordial value of $\delta^{34}\text{S} = 0$ (11). (iii) The mean value of $\delta^{34}\text{S}$ of the river input to the ocean is near +8‰ (12, 13). From our Fig. 2, this mean is:

$$\frac{(+19\text{‰})(1.0 \text{ Emol S/Myr}) + (-16\text{‰})(0.48 \text{ Emol S/Myr})}{(1.0 + 0.48) \text{ Emol S/Myr}} = 7.65\text{‰}$$

(E = exa, 10¹⁸). (iv) The fractionation factor between reduced sulfur and sulfate is 35‰. The mean values of $\delta^{34}\text{S}$ of the sulfide and sulfate reservoirs should differ by the fractionation factor. However, there are large differences between estimates of such mean values, from 33‰ (2) to 40‰ (3). Furthermore, we have changed the present-day ocean from its measured +20‰ $\delta^{34}\text{S}$ to +19‰ in the cycle model of Fig. 2 so that the ocean and the gypsum reservoir are in isotopic equilibrium. A small fractionation factor for sulfate during deposition from ocean water, about 1.5‰ (2), was not considered because of the comparable or larger uncertainties in the sulfide-sulfate fractionation. (v) The isotopic fractionation factor between carbon in organic

matter and in carbonates is taken as 25‰ (3, 14). (vi) The mean $\delta^{13}\text{C}$ of the carbonate reservoir is +0.46‰ (3). Correspondingly, the mean for the organic carbon reservoir is (+0.46‰ - 25‰) = 24.54‰. (vii) The mean $\delta^{13}\text{C}$ of the three carbon-containing reservoirs in Fig. 2—ocean plus atmosphere, carbonates, and organics—is -4.54‰. A value of -5‰ has been suggested for the mantle, or primordial, carbon (11). (viii) The total fluxes of carbon and sulfur from sedimentary reservoirs into the ocean-atmosphere system, as given in Fig. 2, are: 15.7 Emol/Myr for carbon and 1.48 Emol/Myr for sulfur. The ratio of these fluxes is 15.7/1.48 = 10.6, as compared to the ratio of 10.25 that would have been deduced by Veizer *et al.* (3) if they had used our fractionation factor.

It should be clear from the preceding list of parameter estimates and constraints that the proposed Holocene steady-state model has been constructed to be consistent with a large number of rather poorly known parameters. The current model serves in part as a test of the sensitivity of the system to the numbers used, and it points toward those values that are most in need of refinement.

The Phanerozoic isotopic record of sediments shows significant secular changes, although it is not clear whether there are any continuous trends for the entire Phanerozoic. Measured fluctuations in carbon and sulfur isotope values surely represent fluctuations of reservoir sizes and fluxes, changes that perhaps ranged from a small fraction of the model values to those several times greater.

Estimates of the reservoir masses and isotopic compositions of sulfur and carbon, shown in Fig. 2, are compatible with the mean isotopic values of the two elements in the exogenic cycle cited previously: $\delta^{34}\text{S} \approx 0$, $\delta^{13}\text{C} \approx -5\text{‰}$. If at any time in the past there were significant selective removal of either pyrite or organic matter (i.e., of isotopically light sulfur or carbon) from the sedimentary cycle then the mean isotopic composition of the sedimentary sulfur or carbon would have been heavier than the preceding values. For a given mass total of either element in the exogenic cycle, a higher value of δ translates into a higher mass of either gypsum or carbonate (i.e., of the isotopically heavier species).

OPERATION OF THE MODEL

Sulfur

In a system in which ocean and atmosphere assumed to have constant composition, the sum of the two fluxes to the ocean

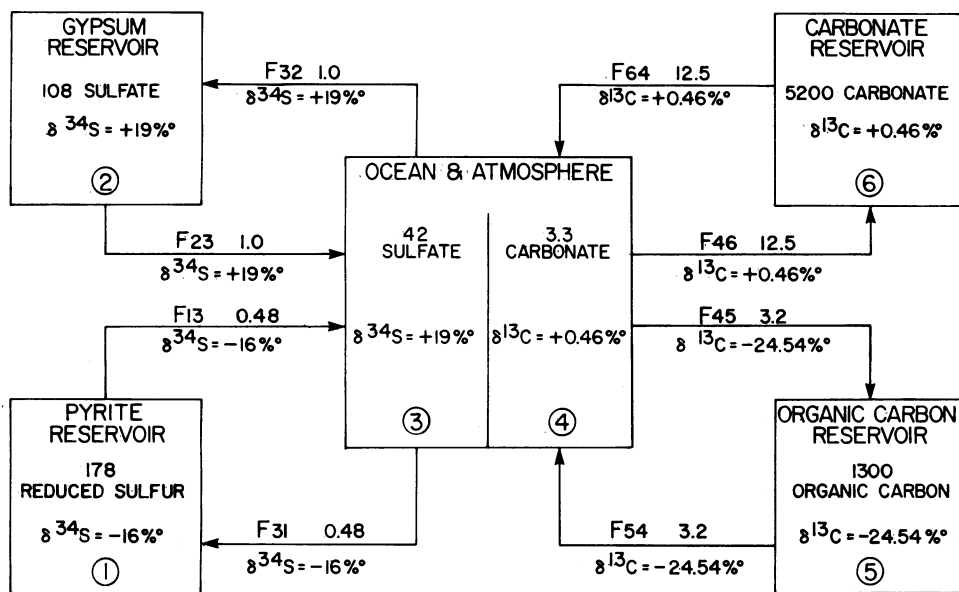


FIG. 2. Holocene steady-state model of global carbon and sulfur cycles. In and out fluxes F are balanced, as in Eq. 2. Reservoirs are in units of 10^{18} moles (Emol); fluxes are in units of 10^{16} moles/million years (Emol/Myr). Isotopic δ values are relative to the standard Canyon Diablo meteorite $\delta^{34}\text{S} = 0$.

is equal to the sum of the fluxes removing material from the ocean to the two sedimentary sulfur reservoirs:

$$F_{13} + F_{23} = F_{31} + F_{32} \quad [2]$$

In the carbon system, because the rate constants F_{ij}/M_i , in which M is the number of moles in the flux, are nearly the same for the carbonate and organic carbon reservoirs, the sum of the fluxes from them to the ocean is virtually constant over the range of the reservoir sizes produced by the model. In the sulfur system, because of the different rate constants, the sum of the inputs from the gypsum and pyrite reservoirs to the ocean has a considerable range, about $\pm 15\%$, during the Phanerozoic.

The sulfate flux out of the ocean is assumed to have the same $\delta^{34}\text{S}$ value as ocean water, and it is assumed that the fluxes into the various sedimentary reservoirs are mixed instantaneously within the reservoir, so that material eroded from each reservoir is always isotopically the same as the rest of the reservoir. This assumption is obviously not true for numerous well-known natural systems. However, the approach here is to idealize the system by introducing such "perfect mixing," with an eye toward examining anomalous results with the mixing problem in mind.

In a cycle model such as the one used here (Fig. 2), an instantaneous change in a steady-state flux of sulfate translates into a change in the isotopic composition of sulfur in ocean water. Our approach has been to develop equations that essentially reverse this: we translate a change in the observed isotopic composition of the sulfate flux out of the ocean into a change in the sulfate flux and, consequently, into changes in the sulfide flux and the sizes of the gypsum and pyrite reservoirs.

The sulfur isotope curve for the Phanerozoic, reported by Claypool *et al.* (2), was slightly recast into a series of linearized sections, as shown in Fig. 3. Then, starting with our steady-state model (Fig. 2) as representative of the Holocene, we used the rate of change in $\delta^{34}\text{S}$ of the ocean from the sulfur isotope curve to compute the reservoir sizes and fluxes backward in time, usually in increments of 10 Myr and sometimes less, when the slope of the isotope curve changed abruptly. After integrating numerically over the time increment, we calculated a new steady-state value for the reservoir sizes S and their isotopic compositions obtained at the end (i.e., beginning on a normal time scale) of the time interval chosen. The steady state was then

perturbed again by using the slope of the $\delta^{34}\text{S}$ -time curve for the next time interval. Table 1 summarizes the results.

Carbon

The model dealing with the carbon system is similar to the one used in computation of the sulfur fluxes and isotopic composition of the reservoirs, except that the carbon system was driven by the computed changes in the sulfate flux out of the ocean (F_{32} in Fig. 2). As shown in Eq. 1, a fixed composition for ocean plus atmosphere suggests that for every 8-mol increase of the size of the sulfate reservoir the organic carbon reservoir must grow by 15 mol. Thus the changes in the sulfur reservoirs were used to compute the changes in the carbon reservoirs, producing, as for sulfur, numbers for fluxes, reservoir sizes, and their isotopic compositions as functions of time. These results are given in Table 2.

Tests of the model

The model can be tested against the measured mean values of $\delta^{13}\text{C}$ of carbonates in individual geological Periods, as compiled

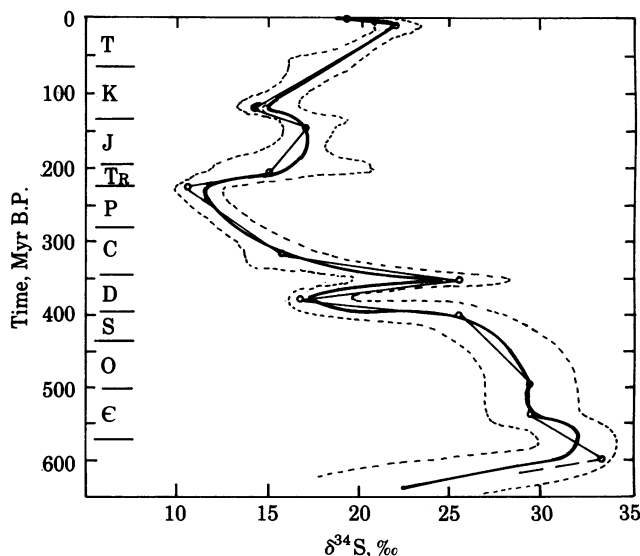


FIG. 3. $\delta^{34}\text{S}$ in sulfates of different geological ages, from ref. 2. Broken contour lines denote the spread of values about the thick curve. The values used in this paper are shown as \circ — \circ .

Table 1. Sulfur cycle: Isotopic compositions, reservoir sizes (S), and deposition fluxes

Time, Myr B.P.	δ , ‰			S, Emol		F, Emol/Myr	
	δ_3	δ_2	δ_1	S_2	S_1	F_{32}	F_{31}
0	19.0	19.0	-16.0	108.0	178.0	1.0	0.48
11.8	22.0	19.2	-16.2	104.6	181.4	0.85	0.61
121.8	14.0	17.4	-15.5	117.0	169.0	1.26	0.28
140	17.2	17.3	-16.0	115.7	170.3	1.10	0.43
210	15.0	16.5	-16.2	122.1	163.9	1.23	0.35
220	10.6	15.7	-15.7	129.3	156.7	1.48	0.14
324	16.1	14.6	-17.3	134.4	151.6	1.21	0.44
350	26.1	15.4	-17.4	118.4	167.6	0.65	0.90
375	17.1	16.4	-16.5	121.8	164.2	1.12	0.45
400	26.1	17.1	-16.6	108.3	177.7	0.64	0.84
500	29.7	21.9	-13.4	73.5	212.5	0.40	0.86
540	29.6	23.5	-12.3	63.7	222.3	0.37	0.82
600	33.6	23.5	-10.9	49.4	236.6	0.15	0.94

Subscripts denote reservoir numbers in Fig. 2. δ_3 values are from Fig. 3.

by Veizer *et al.* (3). Fig. 4 is a plot of these Period means against the values of $\delta^{13}C$ derived from our sulfur-carbon coupled model. The predicted and measured values agree well. Clearly there is much more detail available from the computed curve than from the Period means. The only marked difference in values is for the Permian Period. The Period mean from the computed curve is obviously about $\delta^{13}C \approx +1\%$, whereas the measured mean is $+2\%$. Welte *et al.* (15) reported $\delta^{13}C$ values of organic matter in Paleozoic sediments, in the time interval between about 300 and 520 Myr B.P. The trend of their measured values is similar to the trend of our computed $\delta^{13}C$ curve for carbonates in the same time interval. The values for $\delta^{13}C$ in organic carbon are more negative (15), and they give mean fractionation factors between $+23\%$ and $+27\%$, that is, the difference between the isotopic values of the oxidized and reduced carbon reservoirs in the Paleozoic.

Fig. 5 is a sensitivity test of the model. Two new curves were added to the computed carbon isotope curve. The solid thin line shows the effect of doubling the carbon fluxes of the original steady-state model, as given in Fig. 2; the broken line shows the effect of increasing the isotopic fractionation factor between reduced and oxidized carbon from 25‰ to 30‰. The departures from the first curve are not striking and they indicate that a little juggling of the fluxes and reservoir sizes of the original model, all within the uncertainties of the data, could be used to fit the observed $\delta^{13}C$ values very well.

Table 2. Carbon cycle: Isotopic compositions, reservoir sizes (C), and input fluxes from reservoirs to the ocean

Time, Myr B.P.	δ , ‰			C, Emol		F, Emol/Myr	
	δ_4	δ_5	δ_6	C_5	C_6	F_{54}	F_{64}
0	0.46	-24.5	0.46	1300	5200	3.2	12.5
11.8	-0.4	-24.5	0.5	1294	5206	2.7	13.0
121.8	1.2	-24.6	0.5	1317	5183	3.7	12.0
140	0.1	-24.6	0.5	1315	5186	3.0	12.7
210	0.8	-24.6	0.5	1326	5174	3.5	12.2
224	2.1	-24.6	0.5	1340	5160	4.3	11.4
324	0.2	-24.6	0.5	1349	5151	3.2	12.5
350	-1.7	-24.5	0.5	1319	5181	1.9	13.8
400	-1.5	-24.5	0.4	1300	5200	2.0	13.7
540	-0.5	-24.4	0.4	1235	5265	2.5	13.2
600	-0.5	-24.3	0.4	1191	5309	2.3	13.4

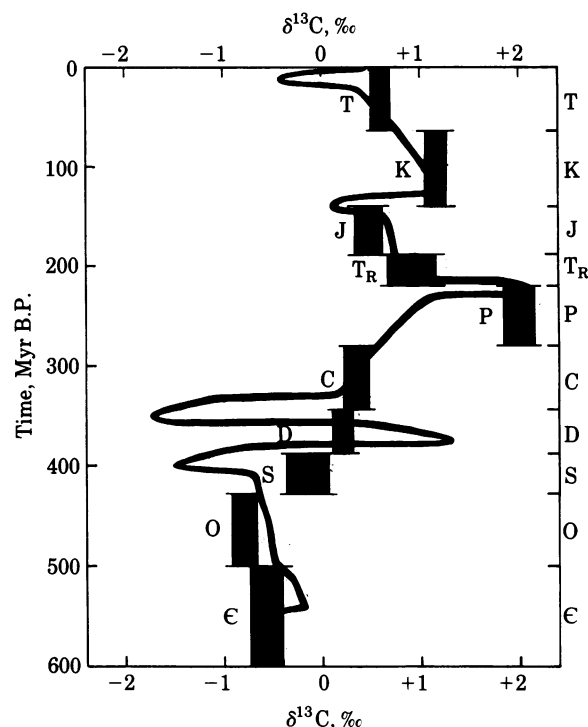


FIG. 4. $\delta^{13}C$ in carbonates (thick curve) computed from the variation in $\delta^{34}S$ with age. Heavy bars are measured mean values of $\delta^{13}C$ for individual Periods, as compiled in ref. 3.

Fig. 6 shows the fluxes of sulfate and organic carbon out of the ocean as a function of time. The sulfate fluxes (Table 1) were computed from the model and the organic carbon fluxes were computed independently by a simpler method from the Period means.

The average rate of change of the organic carbon flux between the Ordovician and Permian (450-250 Myr) is 0.0088 Emol/

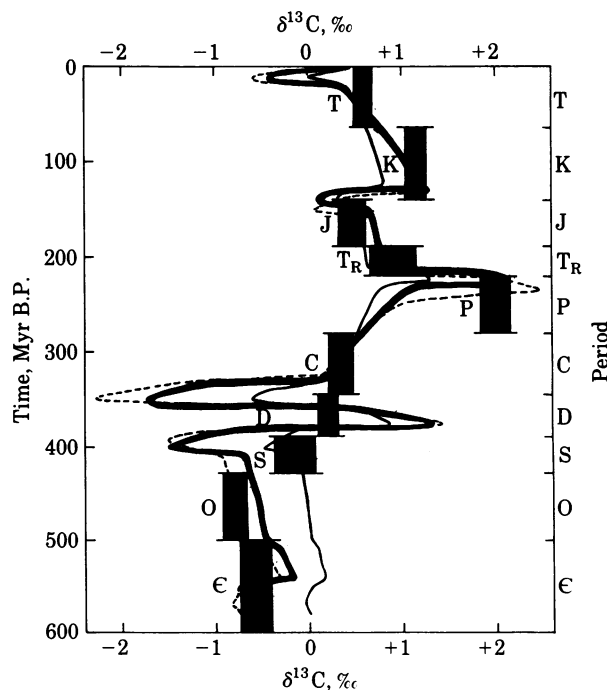


FIG. 5. $\delta^{13}C$ in carbonates, as in Fig. 4. Thin solid line, carbon fluxes double the values shown in Fig. 2; broken line, isotopic fractionation factor for reduction of carbon raised from $\alpha_C = 25\%$ to 30‰.

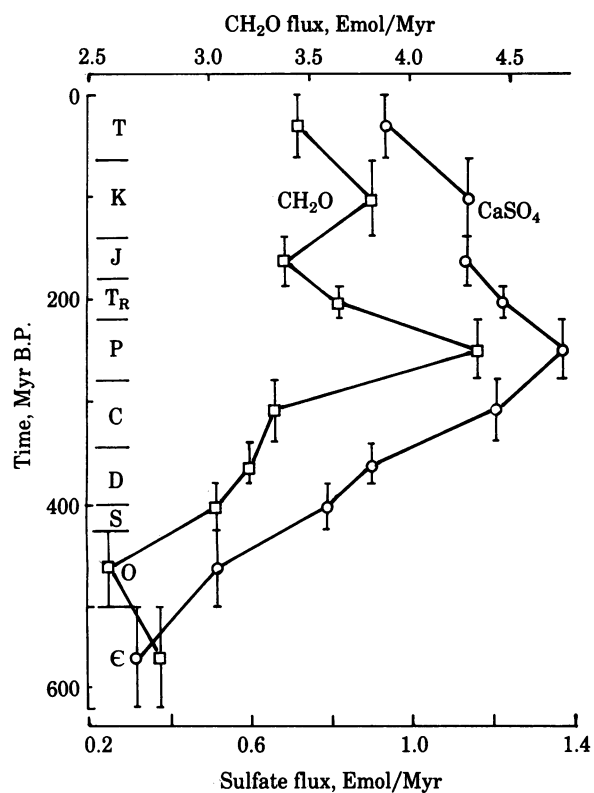


FIG. 6. Variations in the organic carbon and sulfate fluxes from the ocean to sedimentary reservoirs (F_{45} and F_{32}) as functions of age. Carbon fluxes were computed from Period mean values of $\delta^{13}\text{C}$; sulfate fluxes were computed from the model.

Myr^2 , and that of the sulfate flux is $0.0041 \text{ Emol/Myr}^2$, giving the ratio of 2.15 for the flux changes. From the Permian to the Tertiary, the ratio is 2.12. From the flux balance model of Eq. 1, the ratio is $1.875 (=15/8)$. Thus, although the fluxes of sulfate and of organic carbon are not necessarily measures of *net storage* of these substances in sediments, the flux ratios do demonstrate that an increase of 1 mol of sulfate flux from the ocean is accompanied by an increase of about 2 mol of organic carbon going into the sediments. Veizer *et al.* (3) noted that, "This relationship suggests a very simple 'zero-order' model: oxygen pro-

duced by photosynthesis of carbon dioxide . . . is used up by oxidation of pyrite sulfur to sulfate." There are just enough discrepancies and parallelisms between the two flux curves in Fig. 6 to suggest verisimilitude, although only additional measurements will help to explain the discrepancies between the slopes of the curves between the Cambrian and Ordovician, and between the Jurassic and Cretaceous.

Ideas involved in the development here have a long history of evolution: through the years they have involved discussions with many persons, especially R. A. Berner, J. I. Drever, B. Gregor, W. Hoefs, W. Holser, H. D. Holland, C. Junge, I. R. Kaplan, J. Lawrence, F. T. Mackenzie, J. McKenzie, the late E. A. Perry, Jr., E. C. Perry, Jr., T. J. Schopf, and M. Schidlowski. This work was supported by National Science Foundation Grant EAR76-12279 and by Gas Research Institute of Chicago Contract 544-464-0183.

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