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ALTERNATIVE MODELING APPROACHES TO THE GEOCHEMICAL CYCLES OF CARBON, SULFUR, AND STRONTIUM ISOTOPES

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ABSTRACT. Geologic records of isotopic changes in ocean composition present the possibility of unraveling the history of secular changes in the geochemical cycles of carbon, sulfur, and strontium. These records must of course be interpreted, and such interpretations are often based on poorly constrained models. Many assumptions are made in these models, and here some of these assumptions are tested.

The geologic record suggests that the isotopic fractionation of C and S between the reduced and oxidized phases can be approximated as constant, although the envelope of variability is large. This allows for the calculation of burial fluxes of organic C and pyrite S based on isotope balance considerations. On the other hand, these fluxes can be assumed constant; changes in oceanic isotopic composition are then driven by variations in the degree of fractionation. Doing so for sulfur produces an age curve that is reasonably supported by observation whereas for C there is no indication of the required changes in isotopic fractionation in the geologic record. Similarly, changes in the isotopic composition of the weathering fluxes can affect oceanic values, but the changes required to account totally for the isotopic record are excessively large. In general, the conventional interpretation of the C and S isotopic age curves, as reflecting changes in burial fluxes, is favored; however, short-term fluctuations may have been caused by these other effects.

For Sr there is no clear, conventional interpretation of secular variability in oceanic isotopic composition against which to weigh the alternatives. Changes in river input rates and exchange rates at oceanic spreading centers have likely significantly affected the oceanic value. However, changes in stream isotopic composition, reflecting increasing and decreasing contributions from shield regions of the continents to the global riverine Sr flux, appear to present the most consistent explanation for long-term secular changes.

INTRODUCTION

To elucidate the Phanerozoic history of our planet one turns to the geologic record and is immediately faced with frustration: the record is incomplete. The fact that sedimentary rocks are recycled means that information on past environments is lost at a logarithmic rate. Only roughly 5 percent of the sediments deposited in the Cambrian have been preserved to the present day (Garrels and Mackenzie, 1969). In contrast, the stable isotopic compositions of unaltered marine chemical precipitates have the potential of giving us an unbiased and virtually uninterrupted measure of many characteristics of the Earth's surface environment over geologic time. This is the allure of the use of isotopes in

paleoenvironmental reconstruction; one carefully selected sample can be representative of the isotopic composition of the world ocean for a particular instant in Earth history.

Even the best isotopic record has to be interpreted in terms of the causes of isotopic change through time, and, unfortunately, these changes always have multiple causes. A common way to deal with the multiplicity of causes is to construct box models, replete with assumptions and simplifications of the processes that one either knows little about or can parameterize in a simple yet representative way. The models then, especially if they are nonlinear, produce from a given input to the model (the isotopic record of a particular element) an output that is more than just a scaled function of the input.

Modeling of this sort can be considered in the form of a posed scenario: given a clear set of assumptions and the isotopic record of choice, the model calculates changes that the variable of interest undergoes through time. One can have utmost confidence in the model results when they are considered in this way; it is only when an attempt to hindcast reality is made that problems of confidence arise. For then the question becomes "how well does the model encompass and simulate the actual processes being modeled?".

A first step from scenario to reality is an assessment of the assumptions and simplifications made in the model. Typically some parameters are held constant over the course of the model calculation, for it is believed that either they can change little over geologic time or are so complicated that one can never hope to involve them dynamically in the calculation. An alternative approach is to parameterize the variable of interest and calculate the changes in the usually specified parameter necessary to produce the observed isotopic trends. The results of this calculation then answer the question "could reasonable changes in the specified parameter have significantly contributed to the isotopic record?". The first section of this paper will take this approach in an analysis of the commonly prescribed isotopic differences between the burial fluxes of reduced and oxidized carbon and sulfur.

Another common assumption is that higher systems effectively subsume lower systems, so that the latter can be lumped into the former. For example, it is often assumed that the weathering fluxes from particular sedimentary reservoirs are simply proportional to their global sedimentary masses, which are in addition assumed to be homogeneous with respect to their isotopic compositions. As a result of this assumption, the isotopic composition of the weathering flux to the ocean changes only slowly through time; its response time is the residence time of the sedimentary reservoirs, typically on the order of 10^8 yrs. To test this assumption, the isotopic composition of streams will be allowed to vary based on the isotope records to see if unreasonable fluctuations are required.

Sometimes, for example in Sr isotope modeling, one is simply unable to assume confidently a single dominant cause for isotopic

variations. At this stage, then, it is perhaps best to study the possible causes in isolation, assuming that the other processes are fixed, perhaps in steady-state. This will be the approach in studying the possible causes of strontium isotopic variations.

CARBON AND SULFUR ISOTOPE MODELING

The simplest form of C and S isotopic models is the constant-oxygen model of Garrels and Lerman (1984). A diagram of this model is shown in figure 1. Carbon and sulfur are each assumed to be resident in two sedimentary reservoirs, one oxidized (carbonate C, gypsum + anhydrite S) and the other reduced (organic C, pyrite S). The ocean also stores oxidized C and S, with an insignificant quantity of the former and a substantial quantity of the latter.

Weathering fluxes are calculated as first order functions of the reservoir size, and the isotopic composition of all reservoirs is assumed to be homogeneous. Based on an assumption of isotope mass balance, either the pyrite or organic carbon burial rates can be calculated using the sulfur or carbon isotope records, respectively. The other reduced burial flux is then fixed by the assumption that there is no net oxygen production or consumption. Finally, the other isotope curve can be calculated as a check of the model assumptions and results.

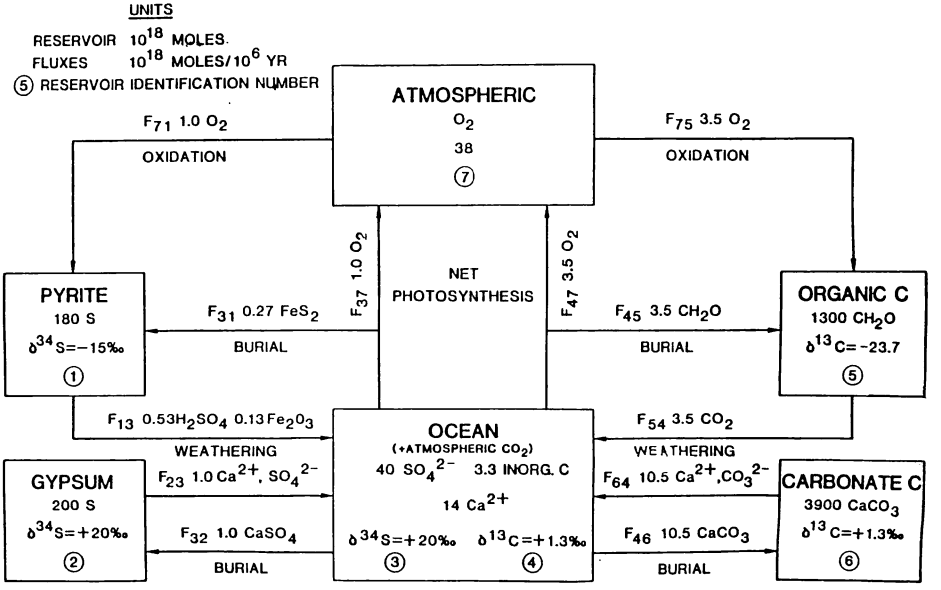

Fig. 1. The coupled sedimentary carbon and sulfur cycles in the assumed Phanerozoic mean steady state (from Kump and Garrels, 1986).

Variation in isotopic fractionation factors.—The Garrels and Lerman model, with modification, has been used by a number of people to investigate long-term changes in organic carbon and pyrite sulfur burial rates and in atmospheric oxygen (Berner and Raiswell, 1983; Lasaga, Berner, and Garrels, 1985; Francois and Gerard, 1986; Kump and Garrels, 1986; Walker, 1986; Berner, 1987). In all cases the normalized isotopic ratio differences between the oxidized and the reduced material being deposited from the ocean ($\Delta^{13}C$, $\Delta^{34}S$) are assumed to be constant. For carbon, this assumption is based on the observation that there is a notable uniformity in the *mean* isotopic compositions of carbonate ($\delta^{13}C = 0$ permil) and organic carbon ($\delta^{13}C = -25$ permil) in preserved sedimentary rocks from 3.5 by old to the present (Schidlowski, Hayes, and Kaplan, 1983), giving $\Delta^{13}C = 25$ permil. For sulfur the assumption of constancy rests on less firm ground, both for a lack of a continuous record of isotopic compositions of pyrite-bearing rocks and for a considerable amount of variability in the record that does exist. Even the carbon isotopic record exhibits a substantial envelope of variability in $\Delta^{13}C$, with a ± 10 permil range in organic C $\delta^{13}C$ for most geologic intervals (Schidlowski, Hayes, and Kaplan, 1983, fig. 7.3).

The model calculations are quite sensitive to $\Delta^{13}C$ and $\Delta^{34}S$. Assuming oceanic steady state

$$F_b = \frac{(\delta_O - \delta_w)}{\Delta} F_w \qquad (1)$$

where

F_b = burial flux of C_{org} or S_{pyr}
δ_O = $\delta^{13}C$ or $\delta^{34}S$ of the ocean
δ_w = mean $\delta^{13}C$ or $\delta^{34}S$ of river input
F_w = total weathering flux (of $C_{org} + C_{carb}$ or $S_{pyr} + S_{gyp}$)

F_b is thus inversely proportional to Δ. An isotopic change in the ocean that would require a doubling of F_b could also be caused by a halving of Δ.

Could the isotopic records of C and S be simply the result of changes in $\Delta^{13}C$ and $\Delta^{34}S$? This question can be addressed by solving eq 1 using the Garrels and Lerman model, if one assumes that organic C and pyrite S burial rates have been constant over the last 570 my. In this case the sulfur and carbon isotope curves (fig. 2) can be used to calculate $\Delta^{34}S$ and $\Delta^{13}C$ (fig. 3).

The calculated ranges in $\Delta^{34}S$ and $\Delta^{13}C$ are similar, from 5 to more than 50 permil. These ranges are large and outside the envelopes of variation discussed above.

The $\Delta^{34}S$ curve bears some resemblance to the isotopic differences between gypsum and pyrite measured by Migdisov, Ronov, and Grinenko (1983). Both curves are in general concave with a minimum in the late Paleozoic. A small value for $\Delta^{34}S$ might indicate that the

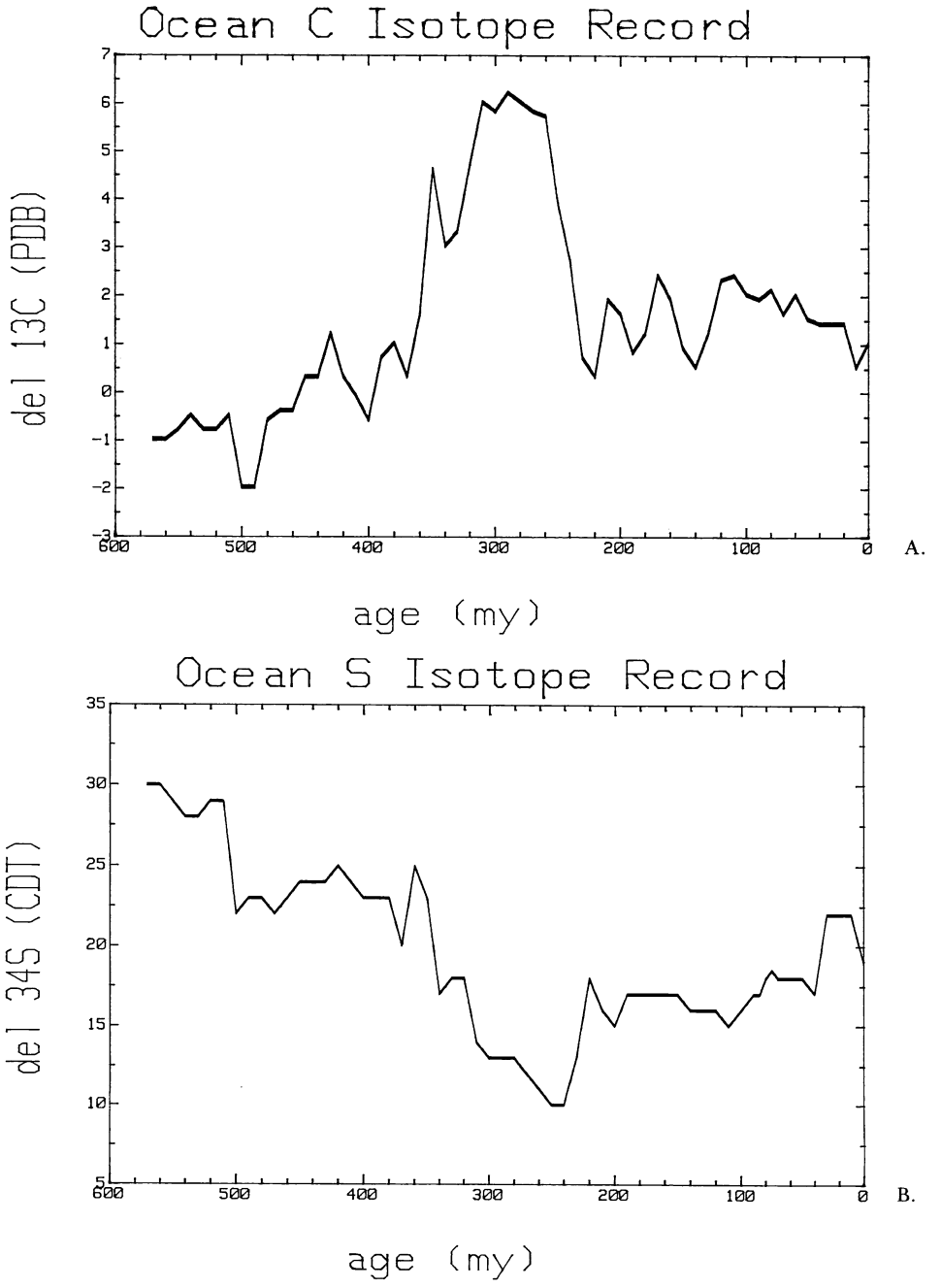

Fig. 2. The stable isotopic composition (A) carbon and (B) sulfur of the ocean through time. From Berner (1987) and references therein.

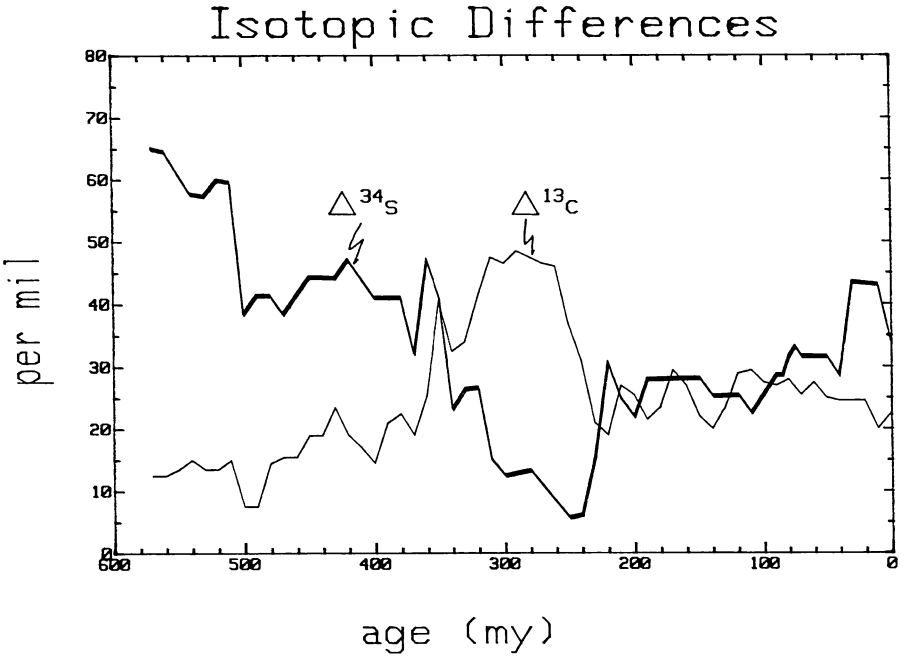

Fig. 3. Calculated changes in the isotopic differences ($\Delta^{13}C$, $\Delta^{34}S$) between the burial fluxes of oxidized (carbonates, sulfates) and reduced (organic carbon, pyrite) sediments as a function of time, assuming constant organic carbon and pyrite sulfur burial rates and using the model of Garrels and Lerman (1984) with the data of figure 2.

conversion of sulfate to sulfide nearly exhausted the reservoir of sulfate available for reduction. A smaller oceanic sulfate reservoir or a less well mixed surface sedimentary layer could have been the reason for this depletion.

In contrast, secular trends in the $\Delta^{13}C$ curve bear no resemblance to any compilation of isotopic differences between Phanerozoic carbonate and organic C (Galimov, Migdisov, and Ronov, 1975; Welte, Kalreuth, and Hoefs, 1975), and its range over Phanerozoic time calculated by the model is much larger than the ranges compiled by Degens (1969). Thus one may conclude that a considerable amount of S but little of the C isotopic variation may have been due to changes in Δ.

An interesting exception to this general conclusion about $\Delta^{13}C$ is the decline shown from the late Cretaceous to the present. Dean, Arthur, and Claypool (1985) and Popp and others (this issue, p. 436) have argued that such a decline may reflect a decrease in atmospheric carbon dioxide partial pressure over this interval. At higher P_{CO_2} the large fractionation associated with the enzymatic carbon fixation in aquatic algal photosynthesis dominates the overall isotopic effect; at lower P_{CO_2}, diffusion of the gas into the plant cell limits the photosyn-

thetic reaction and produces a smaller isotopic effect. Thus $\Delta^{13}C$ between marine carbonates and organic carbon may provide a paleobarometer for P_{CO_2}. The calculated decline in $\Delta^{13}C$ (fig. 3) from 30 to about 23 permil is conceivable given the suggested decline in P_{CO_2} from the Cretaceous to the present (Berner, Lasaga, and Garrels, 1983).

Variation in river isotopic composition.—Eq 1 shows that the isotopic composition of the riverine carbon and sulfur flux strongly influences the calculation of organic carbon and pyrite sulfur burial rates. As discussed in the Introduction, this value changes slowly over the course of a Phanerozoic Garrels and Lerman model run. One may wonder if variations in the geographic distribution of the types of rocks being weathered, or in the intensity of chemical weathering on regional or global scales, may have significantly altered the isotopic composition of streams over this time period.

Eq 1 could be solved for $\delta_w(C)$ by allowing (1) the S isotope curve to determine pyrite burial rates; (2) first order relationships between reservoir sizes and weathering rates in the sulfur cycle; (3) the constant oxygen constraint to determine organic carbon burial rates: and (4) the C isotope curve to determine the relative contributions of organic and carbonate carbon to δ_w (at constant $\Delta^{13}C$). Such a calculation gives reasonable results for the last 200 my but requires negative contributions from organic or carbonate C at other times and is extremely sensitive to initial modeling conditions. This is because the redistribution of carbon weathering contributions also affects the oxygen balance: positive feedbacks reside in this coupling, as described by Berner (1987).

An alternative is to assume that river isotopic compositions have varied due to changes in the isotopic compositions of the fossil organic carbon or carbonate rocks being weathered (independent of their relative weathering rates). For example, the isotopic composition of the organic carbon being weathered today was determined long ago during the deposition and diagenesis of the shales that contain this organic carbon. Heterogeneity in the age of geographical distribution of the shales being weathered could thus cause changes in the C isotopic of streams.

Figure 4A shows the changes in the isotopic composition of streams that would be required to produce the C isotope record, assuming that first-order kinetics govern all weathering processes, that the isotopic composition of the carbonate rocks being weathered is a slowly varying function of time determined by these kinetics, that the sulfur isotope record determines sulfur cycling rates directly and organic carbon burial rates indirectly through the constant oxygen requirement, but that the isotopic composition of the kerogen being weathered is that which satisfies the carbon isotope balance equation.

Figure 4B shows how the change in δ_w is effected, that is by changes in the kerogen δ_w. The range is large but not entirely unreasonable, from -40 to -3 permil. Times of very heavy or very light δ_o require

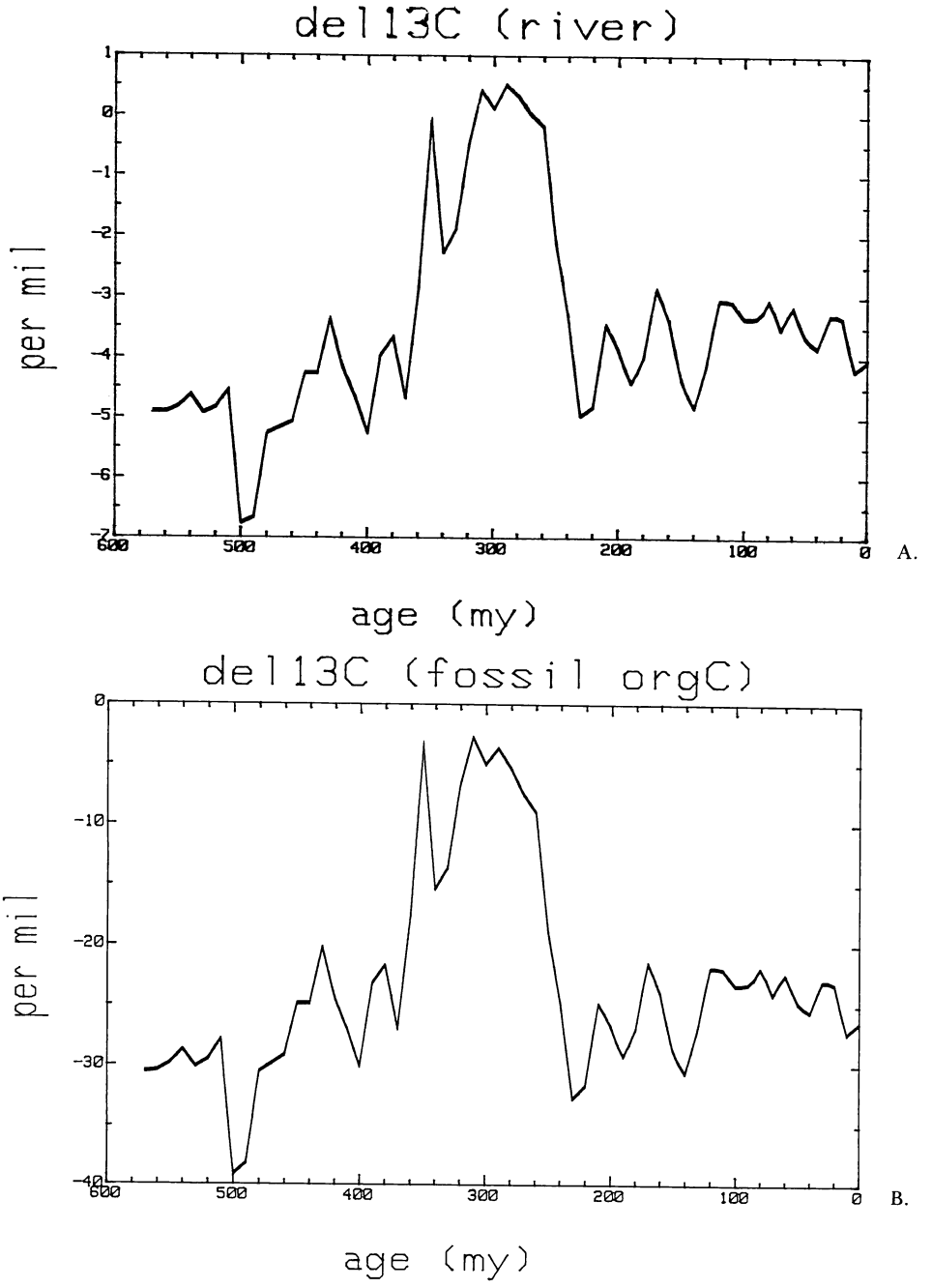

Fig. 4 (A) Calculated changes in the global-mean river isotopic composition as a function of time, assuming (B) rapid changes in the $\delta^{13}C$ of kerogen in shales. Other assumptions detailed in text.

these extreme values and more likely represent times of more or less rapid rates of organic carbon burial than those required to balance the sulfur cycle (times of oxygen production or consumption, respectively).

Summary of carbon and sulfur modeling.—The results of the modeling suggest that a re-evaluation of the assumptions commonly made in carbon and sulfur modeling is justified. Reasonable changes in the usually specified parameter Δ, and more rapid variability in river isotopic composition than is allowed in the Garrels and Lerman type of model, could have significantly influenced the isotopic records of oceanic carbon and sulfur. However, recent work by Berner (1987) demonstrates that rapid recycling of young sediments (which leads to more rapid changes in the isotopic composition of the weathering inputs) does not appreciably change the calculated organic carbon burial rate. Of course, rapid recycling is not the only way to change relative weathering rates of shales, carbonates, and evaporites; regional climatic and tectonic changes could significantly affect the mean isotopic composition of the world's rivers (although coupled changes in oxygen consumption rates would result), as could the isotopic composition of the rocks being weathered. More persuasive are the sediment inventory model calculations of Berner and Canfield (this issue, p. 333) which generate organic carbon burial rates remarkably consistent with those calculated using isotope models. Their results show that burial of reduced C and S is the dominant process controlling the isotopic composition of C and S in the ocean.

STRONTIUM ISOTOPE MODELING

Perhaps one of the best defined isotope records for the Phanerozoic is that of strontium (fig. 5; Burke and others, 1982). Beginning with Spooner (1976) and Brass (1976), there have been numerous attempts to model the strontium isotope record in terms of the important processes that affect the oceanic strontium cycle (Albarede and others, 1981; Holland, 1984; Palmer and Elderfield, 1985; Wadleigh, Veizer, and Brooks, 1985; Chaudhuri and Clauer, 1986; DePaolo, 1986; Hess, Bender, and Schilling, 1986). Here each of these processes will be studied in isolation to assess the range of variation necessary in each of them to account for the temporal changes observed.

The global strontium cycle is depicted in figure 6, with fluxes and isotopic ratios essentially those compiled by Wadleigh, Veizer, and Brooks (1985). The source of strontium to the ocean is from rivers (F_{RO}), where strontium is associated with the dissolved load (groundwater runout may also be significant; see Chaudhuri and Clauer, 1986). The sink for strontium is its deposition with carbonate minerals (F_{OC}). There is no isotopic effect associated with the deposition of strontium from the ocean, so that changes in the rate of this process only affect the size of the oceanic Sr reservoir (M_O) and thus its rate of isotopic response (Kump, 1989).

The isotopic composition of Sr in the ocean (r_O) is determined by the relative rates of input from weathering (with r_R) and exchange

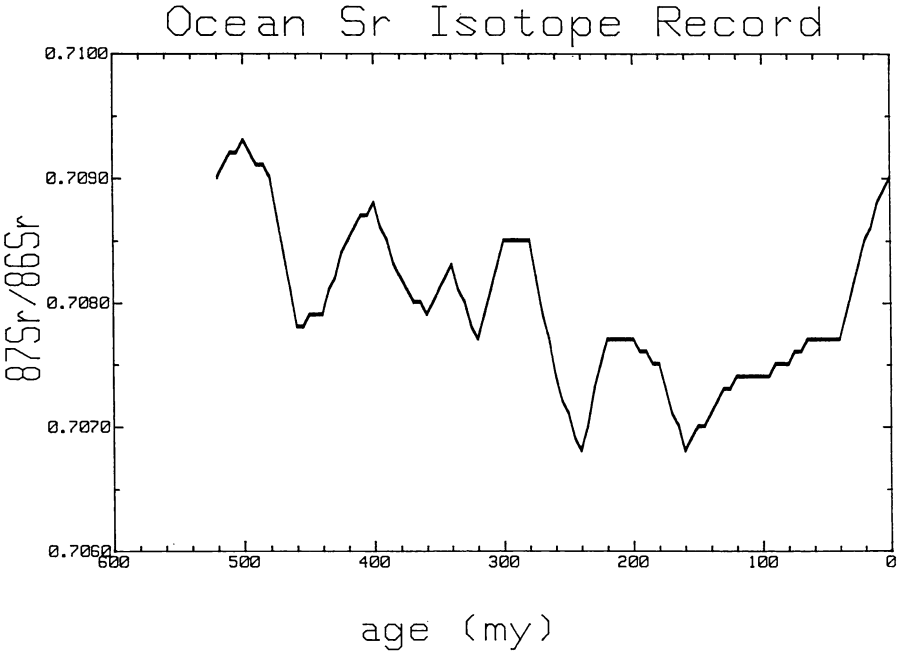

Fig. 5. The strontium isotope-age curve (after Burke and others, 1982).

during hydrothermal cycling of seawater through the mid-ocean ridge system ($F_{OB} = F_{BO}$). The latter process is often assumed to have no effect on the total strontium content of the ocean (Edmond and others, 1979; Elderfield and Greaves, 1981; Albarede and others, 1981); hydrothermal fluids discharging from the ridges are neither depleted nor enriched significantly in Sr, probably because of a combination of low and high temperature hydrothermal reactions (Berndt, Seyfried, and Beck, 1988). However, the isotopic ratios (r_B) of the fluids are reduced to near the basalt value (Albarede and others, 1981). There is a strontium flux from marine porewaters (F_{CO}) due to carbonate diagenesis (Elderfield and Gieskes, 1982). Because this flux returns recently deposited Sr, it acts as a buffer to change in the marine isotopic ratio. Its effect will be addressed separately, and for the other model runs it will be neglected.

The rate of change of the strontium isotopic ratio in seawater for the model (modified from Brass, 1976) is:

$$\frac{dr_O}{dt} = \frac{\left(\frac{1 + r_O}{1 + r_R}\right)(r_R - r_O)F_{RO} - \left(\frac{1 + r_O}{1 + r_B}\right)(r_B - r_O)F_{OB}}{M_O} \qquad (2)$$

This equation can be manipulated so that any one of the variables becomes dependent; the rest are then specified.

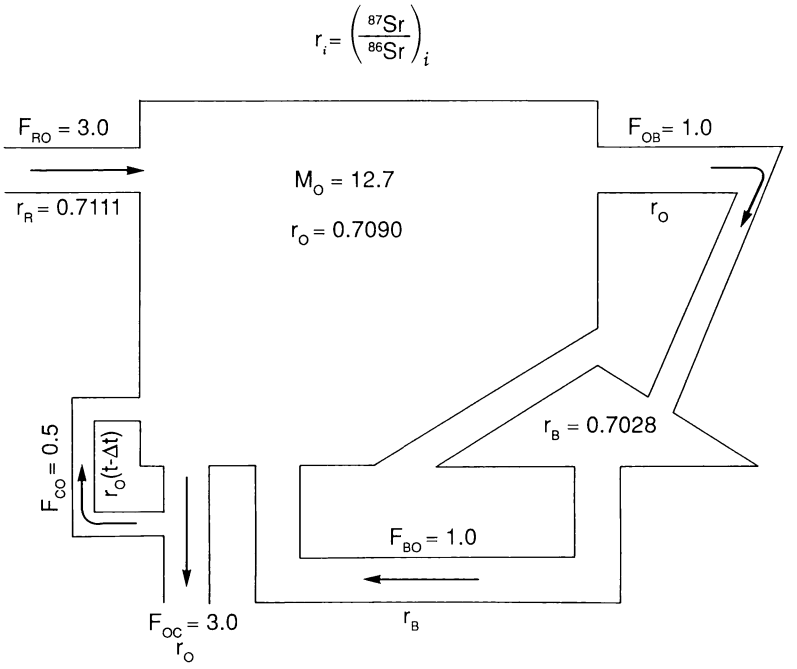

Fig. 6. The global strontium cycle. See text for abbreviations. Fluxes in 10^{10} mol/yr, reservoir size (M_O) in 10^{16} moles. After Wadleigh, Veizer, and Brooks (1985).

Changes in river flux.—If it is assumed that there have been no changes in the rate or isotopic composition of seawater cycling through the ridges and in the isotopic composition of the riverine input through geologic time, then changes in the riverine flux completely determine the Sr isotope age curve. Figure 7 shows the calculated fluctuations in this input rate for the interval from 500 my ago to the Present. The overall Phanerozoic trend is a decrease through the Paleozoic from a flux comparable to today's to one that is about a third of the present-day Sr flux, little change in the Mesozoic, and a montonic increase in the Cenozoic.

These trends are not consistent with geological observations and modeling studies of changes in climate through time. For example, from the Cretaceous to the present, both global temperature and global runoff rates are believed to have decreased (Berner, Lasaga, and Garrels, 1983), despite increased land area. For river fluxes of strontium to have increased, the concentration of strontium in rivers would have had to increase even more, to compensate for the low discharge. The implied increase in chemical weathering rates would be in spite of cooler temperatures and less rainfall. Chemical weathering rates are undoubtedly also tied to uplift and mechanical erosion rates (Holland, 1978), so

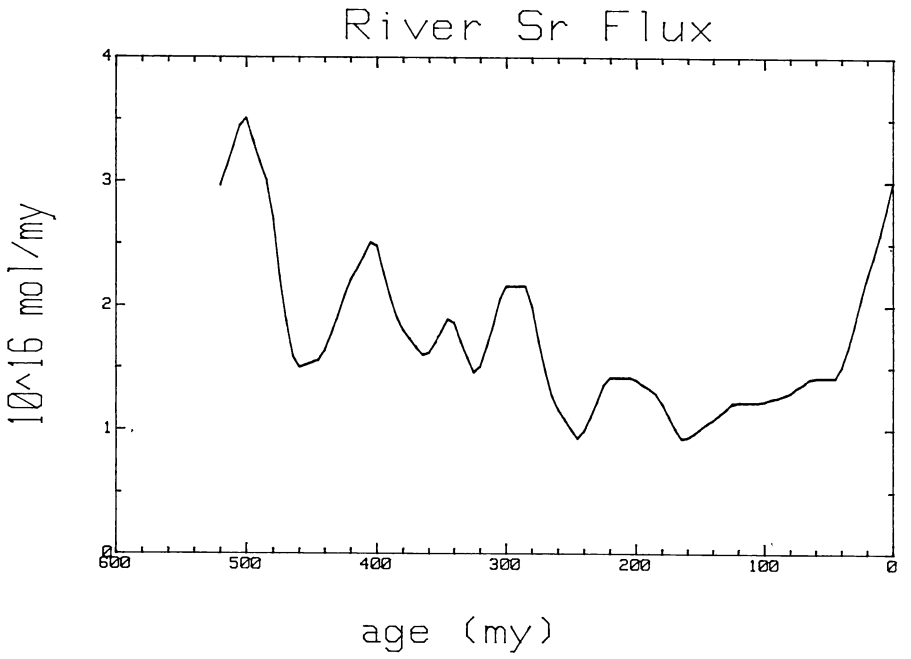

Fig. 7. Calculated changes in the river flux of Sr necessary to produce the isotope curve of figure 5, assuming all other fluxes, isotopic compositions, and reservoir sizes constant.

perhaps the Cenozoic rise in the strontium isotope ratio occurred in response to increased tectonism, related to Alpine and Himalayan orogenies (compare Palmer and Elderfield, 1985; Hess, Bender, and Schilling, 1986).

Non-steady-state oceanic strontium reservoir.—There is no reason to suspect that the present amount of Sr in the ocean is representative of that of the past 500 my, especially if the variability of input rates suggested by figure 7 is representative of the real situation. The removal rate of Sr with carbonate sediments can be approximated as being first order with respect to the amount of Sr in the ocean (assuming a constant carbonate burial rate):

$$F_{OC} = kM_O \tag{3}$$

Then, using the model results of figure 7, for which constant F_{OB}, r_B, and r_R were assumed, the changes in the oceanic Sr reservoir through time can be calculated (fig. 8). The estimated range is from half to about 25 percent greater than today's reservoir size, which, assuming a roughly constant throughput, is also the range in residence times calculated for Sr in the ocean.

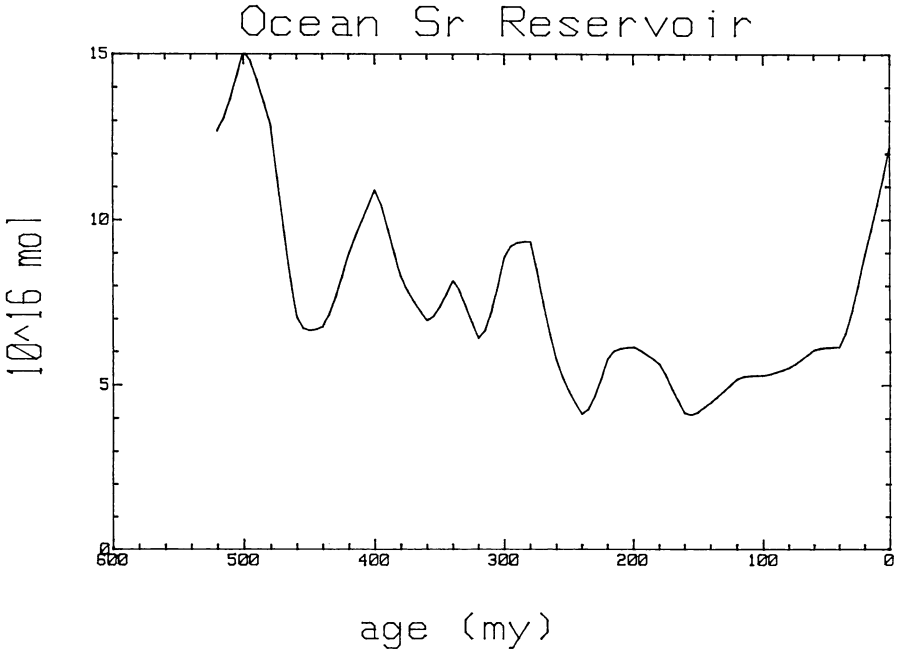

Fig. 8. Calculated changes in the size of the oceanic Sr reservoir (M_O) assuming first order removal rates and the conditions of figure 7.

An independent estimate of the size of the oceanic Sr reservoir can be made on the basis of the absolute value of the rate of change of the isotopic ratio (which is a reflection of the residence time). When M_O is large, the response of r_O to changes in fluxes and their isotopic compositions is damped, whereas when M_O is small, r_O responds rapidly. Such an analysis by Kump (1989) requires small reservoir sizes for the period 25 to 50 my, 175 to 250 my, and 250 to 350 my. These periods are not especially well matched by figure 8, indicating that the simplifications proposed here and perhaps in Kump (1989) fail to encompass the dominant processes affecting oceanic Sr concentrations and rates of isotopic response.

Diagenetic fluxes.—During the early diagenesis of marine carbonate sediments, Sr-bearing carbonate minerals recrystallize into relatively Sr-depleted phases. Sr concentrations in the pore waters increase above oceanic values, and thus there is a diffusive flux of Sr from the sediment to the overlying ocean (Elderfield and Gieskes, 1982; Gieskes, Elderfield, and Palmer, 1986). The isotopic composition of this Sr flux will be determined by that of the sediments, which were deposited at a slightly earlier time.

To test the effect of this flux on the calculations presented here, the diagenetic flux is added to eq 3. The assumed value is 0.5×10^{16} mol/my. For simplicity in the model, the diagenetic flux is assumed to have an isotopic composition that is the mean seawater value for the preceding 20 my. The model can then be configured to calculate the river flux, as above, but now with the diagenetic flux added.

The results are shown in figure 9. There is a small increase in the magnitude of the fluctuations in the calculated fluxes. This increase could have been inferred; essentially the buffering of oceanic change by the diagenetic flux demands a larger change in the river input (the dependent variable) to effect the specified change in oceanic isotopic composition. In reality, the diagenetic flux tends to damp oceanic isotopic fluctuations caused by flux imbalances in the global Sr cycle. But because the flux is small, and because its isotopic composition is very close to the oceanic value, it has a small effect on oceanic isotopic composition.

Changes in river isotopic composition.—Brass (1976) and Palmer and Elderfield (1985) have proposed that variations in the Sr isotope record were due largely to changes in the isotopic ratio of the stream input.

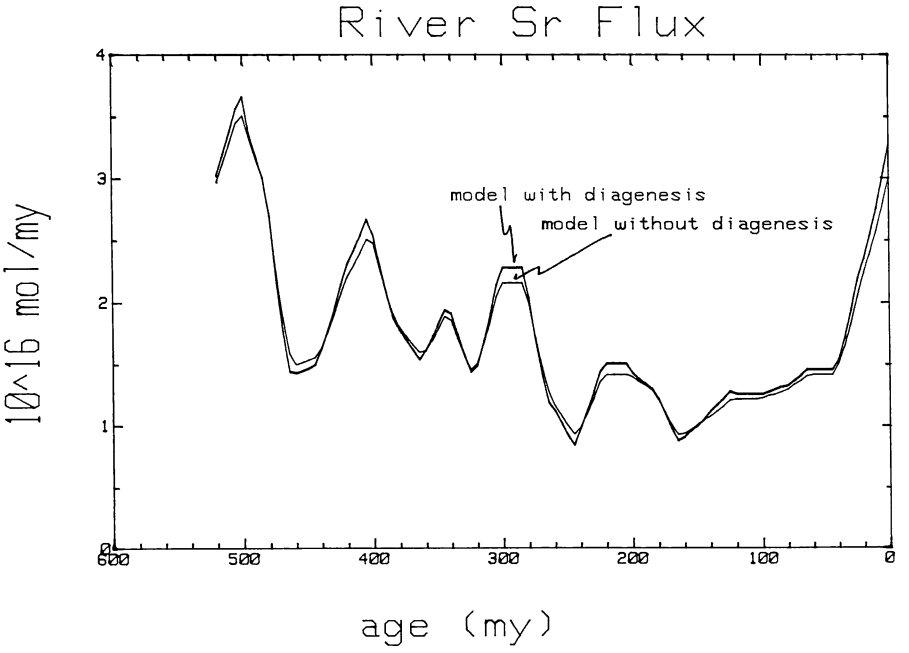

Fig. 9. The effect of the incorporation of a diagenetic flux of Sr on the system described in figure 7.

Such changes would be due to changes in the proportion of the weathering flux due to granitic rocks, whose isotopic ratio is >0.71, relative to the contributions from carbonate rocks ($r \cong 0.708$) or basaltic rocks ($r \cong 0.704$) (after Wadleigh, Veizer, and Brooks, 1985 and references therein).

A calculation of the changes in the river isotopic composition necessary to account for the Sr isotope record can be made using eq 2. Mid-ocean ridge fluxes and their isotopic composition, the river flux of total Sr, and the amount of Sr in the ocean are all held constant. The result of this calculation is shown in figure 10.

The general trend is one of decreasing contributions from granitic rocks through the Paleozoic and a reversal in the Mesozoic to increasing contributions through the Cenozoic (similar to the model results of Brass, 1976). A Paleozoic decline in r_o caused by increasing contributions of carbonate weathering would be consistent with the idea that the Paleozoic transgressions covered granitic regions of the continents with carbonate sediments with distinctly lower r and with other sediments with low Sr contents and isotopic ratios.

Changes in mid-ocean ridge recycling.—Spooner (1976) first suggested that the modern Sr isotopic composition of seawater and changes

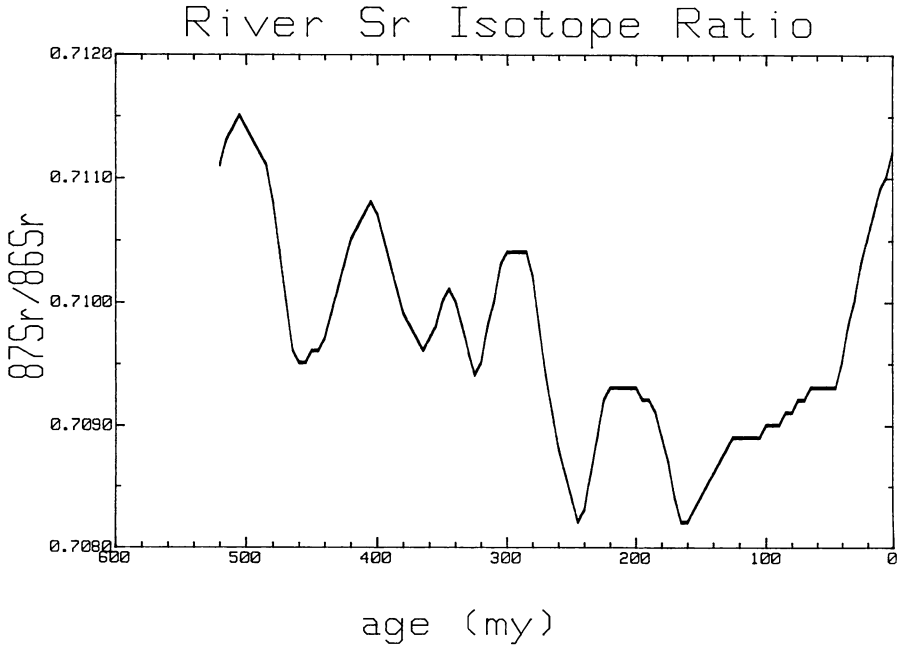

Fig. 10. Calculated changes in the river Sr isotopic composition necessary to produce the isotope curve of figure 5, assuming all other isotopic compositions, fluxes, and reservoir sizes constant.

through Earth history in this value have been significantly affected by isotopic exchange attendant on the recycling of seawater through mid-ocean ridge hydrothermal systems. Recent estimates of world mean r_R require a marine source of non-radiogenic Sr to balance the steady-state system at the present r_O (Waldleigh, Veizer, and Brooks, 1985). The question is whether the Phanerozoic changes in r_O could have been largely the result of changes in the rate of isotopic exchange at the ridges.

Once again, eq 2 can be used with the observed isotope record to solve for F_{OB} through time, assuming everything else constant. The results are shown in figure 11.

In general, what is seen is that calculated ridge recycling rates increase through the Paleozoic and early Mesozoic and then decline from the Cretaceous to the Present. The entire range is from rates similar to today's in the Cambrian to rates three times today's in the Triassic and Cretaceous.

Other geologic monitors of global seafloor spreading activity include volcanogenic sediments and eustatic sealevel (Pitman, 1978). The percent of volcanogenic sediments in the total preserved sedimentary mass (Ronov, 1982) does increase throughout the Paleozoic and

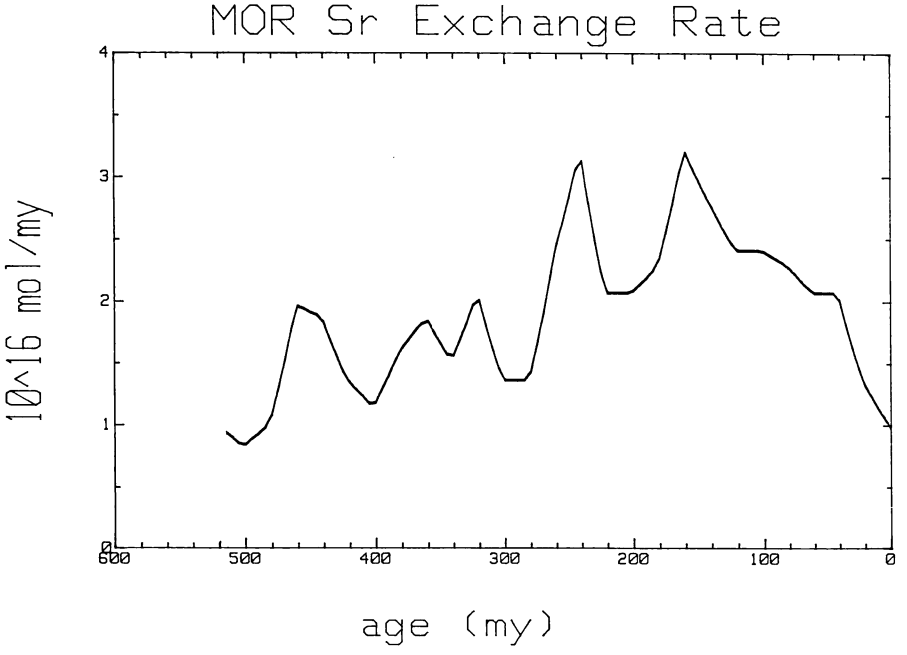

Fig. 11. Calculated changes in the mid-ocean ridge recycling rate necessary to produce the isotope curve of figure 5, assuming all other fluxes, isotopic compositions, and reservoir sizes constant.

decreases from the Cretaceous to the present, tending to support the implications of figure 11. However, the eustatic sealevel curve (Vail, Mitchum, and Thompson, 1977) suggests just the opposite, that spreading rates, if they do indeed dominate the control of eustatic sealevel on long time scales, were high in the early Paleozoic and decreased substantially to the Permo-Triassic lowstand. The inferred Cretaceous sealevel highstand is interpretable in the Sr isotope record, but otherwise figure 11 bears little resemblance to the Phanerozoic eustatic curve.

IMPLICATIONS AND CONCLUSIONS

The primary purpose of this paper is a modest one: to show the range of variability implied by alternative interpretations of the isotope records. This exercise is especially important for understanding the Sr isotope record, for no clear dominant cause has been established for its secular variations. In contrast, the conventional interpretation of the carbon and sulfur isotope records seems secure; major excursions have resulted from coupled and decoupled changes in the rates of organic carbon and pyrite sulfur burial.

Perhaps the most perplexing problem in C-S modeling is the high rate of net oxygen production calculated for the Permo-Carboniferous (Berner, 1987). More than twice the present amount of atmospheric O_2 is calculated to have been produced in about 100 my, apparently without a similar growth in the O_2 sink. This conclusion, however, is based on a model that assumes Δ as constant and F_w as a slowly varying function of time or as a function tied directly to burial via "rapid recycling" (Berner, 1987). Eq 1 shows that isotopic variations could have alternative interpretations. One possibility is that periods of very heavy δ_O imply times of low F_w rather than high F_b, because all the isotope record tells us is the ratio of F_b/F_w (assuming δ_w and Δ are known). If this interpretation were true, the oxygen production problem could be significantly reduced.

Table 1 shows oxygen production rates that result from imbalances in the carbon cycle as a function of $F_w(C)$ consistent with a δ_O of +5 permil and $\Delta^{13}C$ of 25 permil. For each value of F_w, F_b is 40 percent of F_w and twice $F_w(C_{org})$. The oxygen production rate is fixed at 20 percent of

TABLE 1

*Oxygen production rates as a function of C weathering rates**

F_w(total C)	F_b	$F_w(C_{org})$	$F_b - F_w(C_{org})$
30	12	6	6
25	10	5	5
20	8	4	4
10	4	2	2
1	0.4	0.2	0.2

*$\delta_o = +5‰$, $\delta_w(C) = -5‰$, fluxes in 10^{18} mol my^{-1}

F_w, so that as F_w decreases, so too does the oxygen production rate. Thus if in general Permo-Carboniferous chemical weathering rates were low, then the heavy $\delta_O(C)$ values may represent increased proportions but decreased rates of organic carbon burial and only small rates of oxygen production.

Another possible way to lessen the Permo-Carboniferous O_2 production problem is to assume that $\Delta^{13}C$ has varied through time; this alternative was explored in figure 3. To maintain constant O_2, $\Delta^{13}C$ would have had to increase to near 50 permil. This value represents extreme isotopic discrimination for ^{12}C, beyond the predictions of the effects of enhanced CO_2 on photosynthetic fractionation (Popp and others, this issue, p. 436). Smaller increases in $\Delta^{13}C$ (above the Phanerozoic mean) could have contributed partially to the heavy oceanic values of this period, but this would have required higher atmospheric CO_2 pressures than present, whereas geologic evidence suggests that the Permo-Carboniferous was a cool time in Earth history (Frakes, 1979).

Changes in $\delta_w(C)$ could also have contributed to the fluctuations in $\delta_O(C)$ in the Phanerozoic, and heavy $\delta_w(C)$ in the Permo-Carboniferous would mean lowered required rates of organic carbon burial and oxygen production (fig. 4A). This increase would have to have been the result of changes in the isotopic composition of the rocks being weathered (fig. 4B); if it represented a decrease in the weathering rate of fossil organic carbon, the oxygen imbalance problem would only be exacerbated. The large fluctuations in $\delta_w(C_{org})$ shown in figure 4B are simply not substantiated by the measurements available.

Thus the large excursions in δ_O can only in part be due to changes in Δ and δ_w. However, many of the wiggles may be, and it would be unwise to interpret the C isotope record in terms of changes in F_b to that degree of resolution. Because the sulfur cycle must be coupled to the carbon cycle, at least on longer time scales, to prevent excessive fluctuation in atmospheric O_2, these conclusions also apply to interpretations of Phanerozoic trends in $\delta_O(S)$.

There is apparently no single primary cause for Phanerozoic variations in the strontium isotope composition of the ocean. Long term secular changes in river discharge, required if the dissolved Sr load has driven the isotope record, are not consistent with other interpretations of Phanerozoic climate. If mid-ocean ridge recycling rates are dominating the record, then eustatic sealevel variations cannot be primarily determined by spreading rates; for example, the Paleozoic trend is toward decreasing sealevel (implying decreasing spreading rates) but increasing isotopic exchange rates. Changes in the isotopic composition of rivers, determined by the relative contributions of granitic and non-granitic sources, cannot be refuted presently as the major cause of Phanerozoic Sr isotope trends, because so little is known about global Phanerozoic paleogeology. The implication of the model is that the granitic source became less important through the Paleozoic, perhaps as

the shield areas became covered with sediments.[1] Then as sealevel fell, Paleozoic sediments were removed (especially during the Mesozoic), so that through the Cenozoic the shield areas again became increasingly important to the world river Sr flux.

Shorter-term fluctuations in oceanic Sr isotopic composition could have been caused by any of the processes involved. Perhaps the best way to assess the various influences for particular intervals is to consider the implications of couplings to other systems. For example, if river discharge is interpreted to dominate the Paleozoic Sr isotope record, this will have implications for interpretations of all other elemental cycles and for sedimentation patterns. Delaney and Boyle (1988) have used this technique extensively to consider possible causes of Tertiary changes in ocean chemical composition.

This modeling has shown that diagenetic fluxes of Sr have only a minor effect on oceanic Sr isotopic composition. The fluxes are small and have isotopic ratios near the oceanic values. Also, if the river input of strontium or its removal with carbonate sediments has varied through time, then so too has the amount of Sr in the ocean. This has implications for the rate of isotopic response to change, which is inversely related to the reservoir size.

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[1] Work in progress on the paleogeology of the Paleozoic is consistent with this interpretation, as are the determinations of the petrologic composition of the regions of continental erosion by Ronov (1982, fig. 17).

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