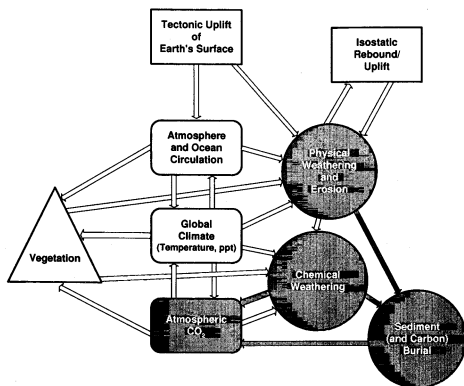


Carbon Cycle Models: How Strong Are the Constraints?

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1. INTRODUCTION

In 1982, Walker *et al.*¹ published a landmark paper suggesting that the evolution of the Earth's climate over 4.5 billion years was controlled by a negative feedback loop involving surface temperature, CO₂, and chemical weathering that moderated the strength of the Earth's "greenhouse effect" over time. As solar luminosity increased over time, surface temperatures on the Earth rose, accelerating the rate of surface chemical weathering reactions (which consumed atmospheric CO₂) resulting in a weaker greenhouse—i.e., a negative feedback system for the Earth's surface temperature, which prevented a runaway greenhouse effect in the face of increasing solar output.

This idea, proposed as a solution to the "faint young sun" paradox, was further developed by Berner *et al.*,² who proposed that climate evolution on multimillion year timescales was controlled by a similar negative feedback loop that balanced the supply of CO₂ to the atmosphere from the Earth's interior and the amount of atmospheric CO₂ consumed by chemical weathering reactions. Because the atmospheric CO₂ reservoir is so small relative to the fluxes in and out, a balance between these fluxes must somehow be maintained within the Earth's C cycle or the atmospheric CO₂ reservoir would quickly build up to unreasonably high values or be depleted to near zero values (runaway greenhouse as on Venus or an icehouse planet as on Mars). Geologic evidence suggests that neither of these scenarios has ever been played out on our planet.

In the more detailed mode of Berner *et al.*² (hereafter BLAG), high rates of seafloor spreading (mantle degassing) in the Cretaceous resulted in a buildup of CO₂ in the atmosphere, a strengthening of the Earth's greenhouse effect, and an increase in surface temperatures. As climate warmed, a proposed increase in global chemical weathering driven by the elevated temperatures and a more vigorous hydrologic cycle acted as a negative feedback preventing the buildup of CO₂ in the atmosphere. As spreading rates fell through the Cenozoic, the CO₂ input dropped, the atmospheric CO₂ level therefore dropped, and surface temperatures dropped. In this scenario, the drop in temperature results in a drop in weathering rates, both of which continue until the input of CO₂ from degassing is balanced by the output of CO₂ from chemical weathering. This paper was significant not only because an entire community of scientists started thinking about long-term climate change in terms of the tectonic C cycle and the greenhouse effect, but because the BLAG model made testable predictions. In particular, if the concept of a global temperature-weathering feedback was correct, then global chemical weathering rates should have dropped through the Cenozoic in concert with falling mantle degassing rates and surface temperature.

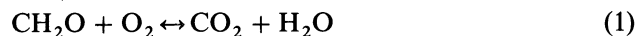
It was the apparent mismatch of this prediction when compared to geologic evidence for weathering rates that led Raymo *et al.*³ to propose that the late Cenozoic uplift and weathering of the Tibetan-Himalayan region led to the drawdown of atmospheric CO₂ and hence to global cooling. This view, however, just traded one set of problems for another; namely, how do you support an enhanced removal rate of C from the atmosphere over the last 40 million years

when the C input from the mantle is presumed to have remained relatively constant? Where does the CO₂ that supports this hypothesized increase in chemical weathering come from once the relatively small atmospheric reservoir is depleted? Lastly, is there a negative feedback to atmospheric CO₂ levels, other than the hypothesized temperature–weathering link, which prevents rapid depletion of CO₂? Three obvious possibilities come to mind: either the evidence for increased chemical weathering has been misinterpreted⁴ (see also Chapter 18); the assumption of constant mantle CO₂ input over the Neogene is incorrect^{5,6}; or another significant flux of C into the atmosphere, which is sensitive to the ocean–atmosphere CO₂ levels (or climate), must exist.

A number of such “alternative” negative feedbacks have been proposed including compensating imbalances in the organic C subcycle^{7,8} and changes in basalt weathering.⁹ However, these proposals are largely theoretical in nature rather than being based on convincing geologic proof of their existence. The point made here is that many researchers use C cycle mass balance models to bolster and illustrate their views, but few new geochemical proxy data have been added to the debate over the last 8 years [important exceptions include Os isotope data (Chapter 17) and phosphorus accumulation estimates].¹⁰ Additionally, geochemical models are sometimes presented as “confirmation” that the system must behave in a certain way to be consistent with mass balance constraints. In this paper, the case of the organic C subcycle is examined in a series of sensitivity tests; the results illustrate how very different interpretations can be supported by the same model with slightly different assumptions for the input parameters. It is concluded that models cannot adequately constrain our understanding of the global C cycle but are useful for guiding further empirical studies.

2. BACKGROUND

The organic C subcycle, which transfers C between oxidized and reduced reservoirs, is summarized by the generalized reaction:



The formation and burial of organic matter (OM) is balanced over geologic time by weathering and oxidation of OM exposed at the Earth’s surface and by metamorphism of OM buried at depth. The flux of C buried in OM, approximately 20–25% of the total C burial flux, is the same order of magnitude as, and indeed is nearly equal to, the flux of C consumed by silicate weathering (~20% of total C burial²). Thus, opposing changes in the organic C cycle have the potential to compensate for imbalances in the rate of silicate weathering (e.g., act as a negative feedback). Indeed, Raymo and Ruddiman⁷ proposed that the increased consumption of CO₂ via silicate weathering suggested by the Neogene Sr isotope record could have been offset by a flux of CO₂ from the increased weathering of OM relative to its burial.

In support of this idea, Raymo and Ruddiman cited earlier work by Lasaga *et al.*¹¹ and Shackleton,¹² which showed that the mean isotopic composition of carbonate buried has dropped over the last 20 million years. Because the formation of OM is accompanied by about a 24–28‰ isotope fractionation relative to the inorganic C reservoir, any change in the relative amount of OM buried versus weathered (all else being equal) would result in a change in the $\delta^{13}\text{C}$ of the inorganic carbonate reservoir. Hence, Lasaga *et al.*¹¹ and Shackleton¹² inferred that the late Cenozoic $\delta^{13}\text{C}$ decrease reflected decreased burial of OM relative to weathering (causing the observed buildup of ^{12}C in the ocean–atmosphere system). Such an imbalance would obviously be driving Eq. (1) to the right and, hence, be adding CO_2 to the atmosphere (where it could be used for silicate weathering).

This interpretation has been challenged by a number of investigators, who suggest that the decrease in mean ocean $\delta^{13}\text{C}$ over the last 20 million years reflects a decrease in the photosynthetic fractionation of OM formed in the ocean, not a decrease in the fraction of OM buried. The most complete treatment of this view (see also Chapter 18) is presented by Derry and France-Lanord¹³ (hereafter DFL96), who argue based on isotopic mass balance constraints that a net addition of C to the sedimentary organic C reservoir occurred over the Neogene. If true, this would further compound the problem of the “missing” CO_2 needed for enhanced silicate weathering. The DFL96 study and the studies of Raymo⁸ and Shackleton,¹² which are further developed here, provide the focal point for the present discussion primarily because they present contrasting views. Another recent study by Compton and Mallinson¹⁴ presents an interpretation of the organic C cycle similar to that of Raymo⁸ and Shackleton.¹² In particular, we need to ask how these similar mass balance models can lead to such different conclusions. How do the assumptions made by these studies differ and are they supported by geological evidence?

3. MASS BALANCE CONSTRAINTS

An excellent discussion of the relevant mass balance equations for the sedimentary C reservoir can be found in the DFL96 study. As described in that and other modeling studies, the change in the size of the sedimentary organic C reservoir with time can be written as

$$dM_{\text{org}}/dt = J_{\text{bur}}X_{\text{orgbur}} - J_{\text{er}}X_{\text{orger}} \quad (2)$$

where J_{bur} is the burial flux of total C (in carbonate and OM) and J_{er} is the erosion flux of same. X_{orgbur} describes the mass fraction of total C buried (or weathered in the case of X_{orger}) as OM. For the purpose of evaluating the transfer of C between the organic and inorganic reservoir, the further assumption is made that the erosional flux of total C equals the burial flux (i.e., $J_{\text{bur}} = J_{\text{er}}$), reducing

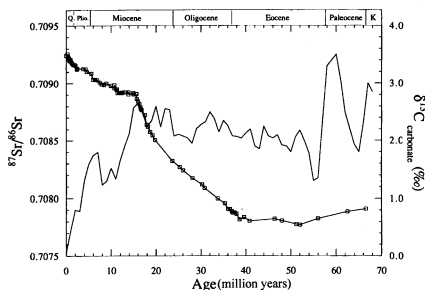


FIGURE 1. Sr isotopic composition of ocean (square symbols) over the Cenozoic from which the estimate of weathering input J_w was derived by Richter *et al.*¹⁸ The solid line with no symbols is the assumed time history of the $\delta^{13}\text{C}$ of buried carbonate based on data collected and published by Shackleton.¹²

Eq. (2) to

$$dM_{\text{org}}/dt = J_{\text{er}}(X_{\text{orgbur}} - X_{\text{orgcr}}) \quad (3)$$

Hence, the growth of, or decline in, the size of the organic C reservoir (dM_{org}/dt) and by extension the flux of O_2 and CO_2 from the sedimentary C reservoir depends on the erosion rate of crustal C and the difference between the fraction of organic C in rocks weathered versus buried.

Because organic and inorganic sedimentary C have very different mean $\delta^{13}\text{C}$ values (by approximately 24–28‰), we can in theory use the $\delta^{13}\text{C}$ value of sedimentary inorganic carbon to constrain both X_{orgbur} and X_{orgcr} with time (see, for instance, Broecker¹³). As discussed more completely in the DFL96 study:

$$X_{\text{orgbur}} = (\delta_{\text{carb}} - \delta_{\text{riv}})/\Delta B \quad (4)$$

and

$$X_{\text{orgcr}} = (\delta_{\text{ave}} - \delta_{\text{riv}})/\Delta E \quad (5)$$

where δ_{carb} is the isotopic composition of carbonate removed from the ocean at time t and is given by the data of Shackleton¹² in most studies (Fig. 1). Here, the

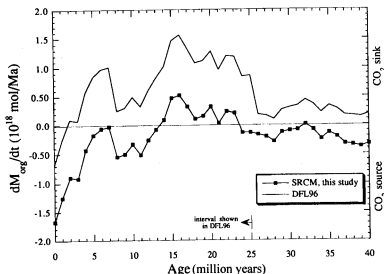


FIGURE 2. Two possible scenarios for the changes in the size of the sedimentary organic C reservoir over the Cenozoic. They approximate (nearly exactly) the dM_{org}/dt history proposed by Derry and France-Lanord¹³ (DFL96) and that derived or implied by the studies of Shackleton,¹² Raymo,⁸ and Compton and Mallinson¹⁴ (SRCM, this study). When the growth of the sedimentary organic C reservoir is positive, the organic C cycle acts as a sink for atmospheric CO_2 (and visa-versa for negative net growth rates).

data have been interpolated at 1-million-year increments; δ_{iv} is the assumed isotopic composition of all C inputs to the ocean; and ΔB is the mean isotopic difference between carbonate and OM deposited at time t (controlled primarily by the magnitude of the photosynthetic fractionation factor). In the equation for X_{org} , δ_{av} describes the mean isotopic composition of carbonate rocks weathered through time, while ΔE is the mean isotopic difference between carbonate and OM being weathered.

Using these five parameters and an assumption about the burial/erosion rate, one can evaluate dM_{org}/dt and determine whether the organic C sedimentary reservoir has increased or decreased in size over the Neogene. Two such calculations are shown in Fig. 2 with the assumed values upon which each calculation was based shown in Table 1. The curve labeled "DFL96" closely approximates a calculation by Derry and France-Lanord,¹³ differing only in that a slightly different time history for J_{er} was assumed. The curve labeled "SRCM" closely reflects the time history of dM_{org}/dt implied by or calculated in the studies of Shackleton,¹² Raymo,⁸ and Compton and Mallinson.¹⁴ The climatic implications of the two curves shown in Fig. 2 are very different. In the DFL96 curve the organic C sedimentary reservoir is acting as a sink for atmospheric CO_2 throughout the last 40 million years (with the exception of the last 2 million years). By contrast, the second curve (SRCM) suggests that the organic C

TABLE 1. Parameters Used for Estimates Shown in Fig. 2

	DFL96	SRCM, this study
J_{er}^a	Variable	Variable
δ_{riv}^b	-5.0‰	-3.8‰
δ_{org}^b	1.8‰	2.0‰
ΔB^b	28.0 to 24.5 to 23.5‰	28.0 to 23.5‰
ΔE	28‰	25‰

^aSimilar weathering rate histories (after Richter *et al.*¹⁶) are used for J_{er} in both cases shown above.

^bThe DFL96 value for ΔB decreases in two steps over 40 million years (at 25 and at 7 Ma) while SRCM, this study, assumes a continuous decrease over same 40 million year interval.

subcycle acted as a source of CO₂ to the atmosphere for a large part of the Neogene. In the following section, the sensitivity of the dM_{org}/dt calculation to each of the five parameters in the model is examined.

4. SENSITIVITY TESTS

In this section, the value of each parameter tabulated in Table 1 is systematically changed and dM_{org}/dt recalculated. For each parameter investigated, all parameters other than the one of interest are held at the values given for SRCM in Table 1.

4.1. Rate of Sedimentary Cycling (J_{er})

As mentioned earlier, the magnitude and direction of weathering rate changes over the Neogene are at the root of the controversy over BLAG-type models. Have chemical weathering and erosion rates increased, decreased, or remained constant over the last 40 million years? More to the point, how does this uncertainty affect estimates of dM_{org}/dt inferred from $\delta^{13}C$ records? The answer is: not by much. As pointed out by DFL96, changes in weathering rates act to amplify (or dampen) existing imbalances in the transfer of C between the oxidized and reduced reservoirs.

In Fig. 2, both scenarios assume the same time history for J_{er} (shown in Fig. 3; note that this time history for J_{er} is slightly different from that used but not tabulated in DFL96). Hence, different assumptions about this parameter cannot be the cause of the difference between the two scenarios shown in Fig. 2. The weathering rate used in Fig. 2 was derived by scaling J_{er} to the change in river Sr flux calculated by Richter *et al.*¹⁶ (Fig. 3) such that the present weathering flux value is approximately equal to the modern C burial flux estimate of Wilkenson and Algeo.¹⁷ In Fig. 4, dM_{org}/dt is also calculated with two additional weathering rate assumptions: specifically, a constant weathering rate of 12.5×10^{18} moles/

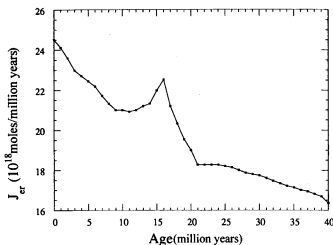


FIGURE 3. The assumed weathering rate J_{er} , which was scaled to the estimated river flux of Sr as determined by Richter *et al.*¹⁸

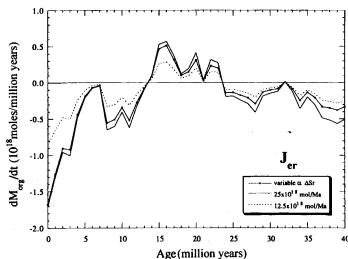


FIGURE 4. Influence of variations in J_{er} on dM_{org}/dt . A low constant weathering rate and a high constant weathering rate are shown for comparison to the Sr-derived rate shown in Fig. 3.

million years and a constant rate of 25×10^{18} moles/million years (all other parameters are as assumed by SRCM, this study, in Table 1). Clearly, at higher weathering rates any imbalance in the partitioning of C between the oxidized and reduced reservoirs is amplified. The crossover points between net positive and net negative growth of the sedimentary organic C reservoir do not change from the variable weathering rate assumption.

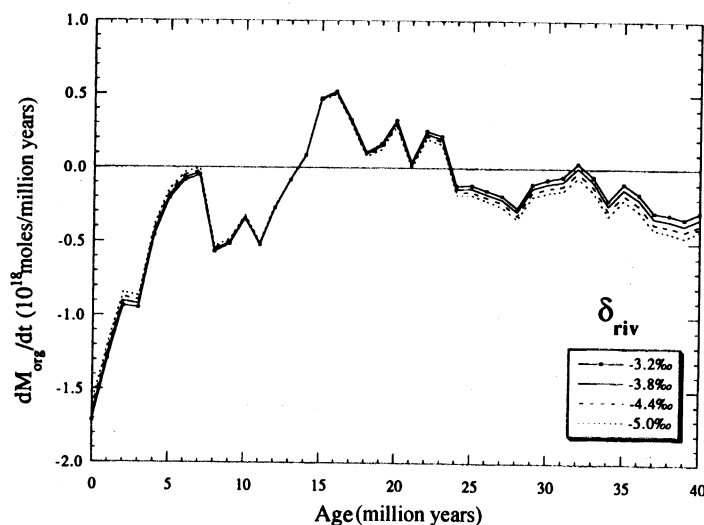


FIGURE 5. Influence of variations in δ_{riv} on dM_{org}/dt .

4.2. River Isotopic Value (δ_{riv})

The calculation of dM_{org}/dt shown in Fig. 2 is also relatively insensitive to the assumed value of the $\delta^{13}C$ input to the ocean (δ_{riv}). In Fig. 5, dM_{org}/dt is shown for four assumed values of δ_{riv} . The -3.8‰ value is after Garrels and Lerman,¹⁸ while the -5.0‰ value (assumed by DFL96) is after Craig.¹⁹ Two other values, -3.2‰ and -4.4‰ , were chosen arbitrarily (although the -4.4‰ value is that used by Garrels and Perry²⁰). The assumptions for the value of this parameter cannot explain the differences between the two scenarios shown in Fig. 2.

4.3. Mean Isotopic Composition of Sedimentary Carbonate Reservoir (δ_{ave})

To calculate the fraction of C eroded as OM [X_{org} , Eq. (2)] one needs an estimate for both the average $\delta^{13}C$ of the sedimentary carbonate rocks undergoing weathering (δ_{ave}) as well as the relative isotopic offset of the OM being weathered (ΔE). The value of δ_{ave} is estimated from the observed variations in the $\delta^{13}C$ of marine carbonates over 600 million years (Fig. 6), often adjusted for the long residence of carbonate rocks and/or the age-mass distribution of rocks (e.g., DFL96). DFL96 assumed 1.8‰ for this parameter. Compton and Mallinson¹⁴ use a slightly higher estimate (closer to 2.1‰), while this study assumes 2.0‰ (Table 1). Any of these values would be a reasonable assumption given our imperfect knowledge of the geologic record (although assuming a single unchanging value is probably an oversimplification as it is unlikely that δ_{ave} has been constant over 40 million years).

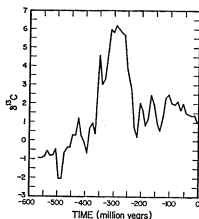


FIGURE 6. The $\delta^{13}\text{C}$ of carbonate deposited over the Phanerozoic (reprinted from Lasaga²⁹).

The value chosen for δ_{ave} has a relatively significant effect on dM_{org}/dt (Fig. 7). All else being constant, when 1.6‰ is used for δ_{ave} , the sedimentary organic C reservoir is growing or constant for all but 12 of the last 40 million years. By contrast, when 2.2‰ is used, the organic C reservoir decreases in size for all but 6 million years. The choice of 1.8‰ (DFL96) and 2.0‰ (SRCM) produces intermediate results accounting for some, but not all, of the difference between the two curves shown in Fig. 2.

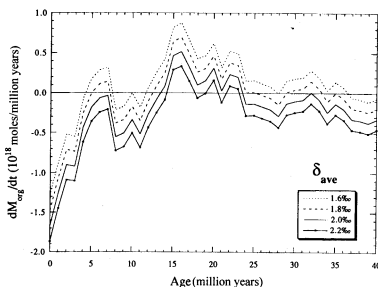


FIGURE 7. Influence of variations in δ_{ave} on dM_{org}/dt .

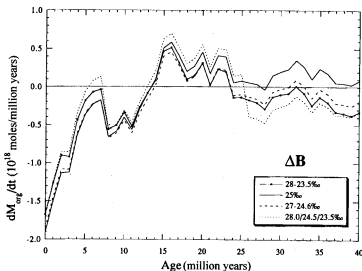


FIGURE 8. Influence of variations in ΔB on dM_{org}/dt . In the last case (dotted) the value for ΔB is stepped down at 25 million years and at 7 million years (after DFL96). In the other two variable ΔB cases (dashed line and solid line with squares), the change indicated occurs linearly over the interval shown.

4.4. Mean Isotope Fractionation between Carbonate and OM Being Buried (ΔB)

The choice of ΔB , the isotopic fractionation between carbonate and OM being buried at time t , has less of an effect on the calculation of dM_{org}/dt than the choice of δ_{org} . Figure 8 illustrates the influence of different assumptions for ΔB ; these assumptions range from constant at 25‰ (e.g., Shackleton¹²) to three more likely scenarios, a gradual decrease from 28 to 23.5‰, a gradual decrease from 27 to 24.6‰, and a stepped decrease from 28 to 23.5‰ (as in DFL96). The latter three scenarios appear to be supported by the data of Popp *et al.*²¹ which suggest that a pronounced decrease in ΔB has occurred since the late Eocene. The conclusion of DFL96 that dM_{org}/dt depends "significantly on the timing of the change in ΔB " is not supported by the sensitivity tests shown in Fig. 8. In fact, the major cause of the difference between the two scenarios shown in Fig. 2 is the value assumed for a related variable, ΔE , as discussed below.

4.5. Mean Isotope Fractionation between Carbonate and OM Being Eroded (ΔE)

As shown in Fig. 9, different assumptions for the isotope fractionation between organic and inorganic reservoirs undergoing weathering (25‰ vs. 29‰) are the major reason for the difference between the two scenarios shown in Fig.

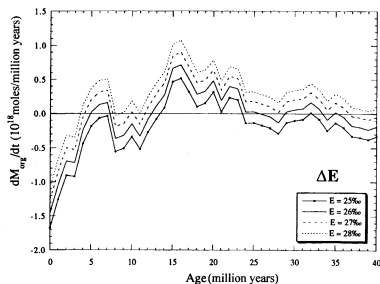


FIGURE 9. Influence of variations in ΔE on dM_{org}/dt .

2. Shackleton,¹² Raymo,⁸ and Compton and Mallinson¹⁴ all assumed a value of 25‰, while DFL96 assumed a value of 28‰. To determine this value exactly, one would need to know the age of all C-rich sediment being eroded at any specific time as well as its isotopic content. It is also unlikely that ΔE would be constant with time; for instance, the current Tethyan-Himalayan orogeny is probably associated with the uplift and weathering of late Mesozoic and early Cenozoic formations, while the early Cenozoic may have been dominated by the weathering of early Mesozoic formations or terrain uplifted during the widespread orogenies of the Paleozoic era.

An early attempt to constrain the isotopic composition of buried OM was made by Craig,¹⁹ who determined that modern land plants showed a mean $\delta^{13}\text{C}$ value of -25‰ (Pleistocene fossil wood was -24‰). Further, coal values from the Pennsylvanian to Pleistocene showed a mean $\delta^{13}\text{C}$ of -24‰ while slate and shale samples from Precambrian to Recent showed a mean $\delta^{13}\text{C}$ value of -28‰ . Craig also estimated that the mean carbonate $\delta^{13}\text{C}$ over the Phanerozoic was 0‰ . It was from these results (in particular the estimate for modern land plants) that the typically assumed value of -25‰ for ΔE was derived. A follow-up study by Degens²² showed slightly modified results (based on a much larger data base); shales and sandstones had a mean $\delta^{13}\text{C}$ value of -26‰ while coals had a mean isotope value of -25‰ . He also found the mean carbonate $\delta^{13}\text{C}$ to approximate 0‰ , implying a ΔE value between 25 and 26‰ .

Since these early studies, additional field and laboratory work, in particular by Lindh,²³ has suggested that mean carbonate values were actually higher over

much of the Phanerozoic, averaging about 1.5‰ over the last 200 million years but ranging between -2 and +6‰ over the last 600 million years (Fig. 6). By the late 1980s geochemical models of the C cycle were using these higher values for δ_{ave} but still assumed 25‰ for the organic-inorganic fractionation (e.g., they did not adopt a corresponding increase in the value of ΔE).

More recent analytical studies of ancient OM^{21,24} suggest that ΔE could be much larger (e.g., closer to 28‰ than 25‰). Lewan²⁴ found two distinct types of OM preserved over the Phanerozoic; a more abundant class with typical $\delta^{13}C$ values of -28 to -29‰ and a less abundant type with heavier values around -22‰. Very light $\delta^{13}C$ values were also found by Popp *et al.*²¹ for late Mesozoic kerogens. Both studies found the heavy $\delta^{13}C$ OM concentrated in sediments younger than 25 million years of age. If one assumed that the bulk of OM weathered today was buried at -28‰, then this would imply typical ΔE values as high as 30‰. However, the disagreement between average Phanerozoic OM $\delta^{13}C$ values found by Degens²² and Lewan²⁴ remains as an unresolved issue. We still may not have a representative survey of the $\delta^{13}C$ of OM contained in the Earth's crust, and subsequently weathered, over geologic time.

5. DISCUSSION

From the above sensitivity tests, one can see that the first-order structure of all model-generated curves follows the basic form of the Shackleton¹² $\delta^{13}C$ of carbonate record. The assumption one makes for the magnitude of the river input (e.g., Richter's Sr curve¹⁶) imprints a longer-term modulation to model estimates. The sign of dM_{org}/dt , which reflects whether the organic C reservoir is acting as a net source or sink of CO₂ to the atmosphere, depends most heavily on the values assumed for ΔE and δ_{ave} . Both of these variables are determined from accumulated $\delta^{13}C$ measurements of Phanerozoic sediments, although the most recent systematic study²⁴ was done over 10 years ago. Given the apparent discrepancies among different studies (e.g., Lewan²⁴ versus Degens²² and Craig¹⁹) and the importance of these data to understanding the mass balance of C, it is imperative that these data be reassessed. For instance, if one assumes 28‰ for ΔE and 1.5‰ for δ_{ave} , one would observe an increase in the size of the organic sedimentary reservoir (and therefore net removal of CO₂ from the atmosphere) for all but roughly the last 3 million years. By contrast if one assumed δ_{ave} was 2.5‰ instead (and $\Delta E = 28‰$), then dM_{org}/dt would be negative for most of the last 13 million years (and therefore the organic C reservoir would have acted as a source of atmospheric CO₂ since the mid-Miocene). The implications of each scenario for Neogene climate change are clearly different.

In addition, this study has assumed that the $\delta^{13}C_{carb}$ record shown in Fig. 1 is accurate. In fact, a 0.1‰ change in this $\delta^{13}C$ value would result in a change in dM_{org}/dt of just under 0.1×10^{18} moles/million years. Because Compton and Mallinson¹⁴ used a slightly different $\delta^{13}C_{carb}$ record in their model, they did not observe a late Miocene increase in the burial of OM relative to erosion, as seen

in both of the studies shown in Fig. 2. The mean $\delta^{13}\text{C}$ of carbonate buried in the Cenozoic is thus another data set that should be evaluated and updated.

An observation on which most agree is that the observed photosynthetic fractionation factor (ΔB) has decreased over the last 60 million years²¹ and that this decrease was most likely driven by a decrease in ocean-atmosphere CO_2 levels (see also Chapter 13). If one assumes relatively high values for ΔE , suggested by Lewan's compilation of Phanerozoic data,²⁴ then the size of the organic sedimentary reservoir would appear to have increased, rather than decreased, over much of the Neogene. Such a shift may have been due to more effective OM burial associated with increased clastic fluxes.²⁵ However, net burial of organic matter would not only lead to a drop in atmospheric CO_2 but would require an additional CO_2 source to support the excess OM burial. An obvious source is a decrease in the rate of silicate weathering. However, the simplest interpretation of the $\delta^{87}\text{Sr}$ data suggests increased silicate weathering.^{3,7-9,14,16,26} Further, the Os isotope data (Chapter 17) implies increased chemical weathering rates over the Neogene (because it seems unlikely that just organic-rich deposits would undergo enhanced weathering). Lastly, could the pronounced increase in clastic erosion observed for the late Cenozoic^{27,28} have occurred without an accompanying increase in chemical weathering (Chapter 14)? If not, we still have a mass balance problem for C.

In conclusion, I suspect we do not even know the sign, over the last 40 million years, of one of the largest fluxes in the global C cycle. The geochemical mass balance models are best used to make testable predictions and help focus data collection efforts. Because they can only mirror our own incomplete understanding of the Earth's geochemical cycles, it is unclear whether they provide any important "constraints." They cannot provide a constraint if their underlying assumptions are false or even slightly inaccurate. Yet, luckily, some of the most important, and most uncertain, parameters in C cycle models can be measured. Data collection has not kept up with modeling efforts in this field and more data, not more models, are what is needed.

Acknowledgments

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