

Neogene growth of the sedimentary organic carbon reservoir

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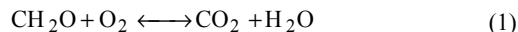
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Abstract. We develop a recycling model using $^{13}\text{C}/^{12}\text{C}$ mass balance for net growth/loss of the sedimentary organic carbon (C_{org}) reservoir, and apply it to the Neogene bulk marine carbonate $\delta^{13}\text{C}$ record. The model allows for variations in photosynthetic fractionation factors, carbon cycling rates, and the isotopic composition of riverine carbon inputs to the oceans. The sign of the net flux term is controlled by the difference between fractional C_{org} burial and fractional C_{org} weathering, independent of any variations in carbon cycling rate. These terms are in turn estimated from the carbon isotope mass balance of newly deposited and weathered sediments, respectively. The magnitude of the net flux is sensitive to the global carbon cycling (erosion/deposition) rate, which may be estimated by the use of the records of radiogenic isotopic variations (Nd, Sr) in paleoseawater. A key observation and input to the model is that photosynthetic carbon isotope fractionation by both marine algae and terrestrial plants has decreased during the Cenozoic. Incorporating time-dependent carbon isotope fractionation into the model shows that the sedimentary C_{org} reservoir has grown throughout most of the Neogene, even as marine $\delta^{13}\text{C}$ values fell after 14 Ma. A similar result is obtained if the variation in the marine $\delta^{13}\text{C}$ record is largely caused by changes in the carbon isotopic composition of river fluxes to the oceans, rather than changes in the organic/inorganic ratio of output to the burial sink. The growth of the sedimentary organic carbon reservoir requires that the Neogene sedimentary carbon cycle was a net source of O_2 and a net sink of CO_2 to the atmosphere, at least until the Plio-Pleistocene. As a consequence, Neogene CO_2 consumption by silicate weathering cannot be balanced by oxidation of sedimentary C_{org} , placing a significant constraint on global carbon balance models. A related prediction of our model is that atmospheric O_2 levels rose during the Neogene.

Introduction

Over geologic time, the burial and erosion of sedimentary organic carbon exert a primary control on the redox balance of the ocean and atmosphere [Garrels and Perry, 1974; Junge *et al.*, 1975; Walker, 1977; Holland, 1984; Budyko *et al.*, 1985; Berner and Canfield, 1989]. The net difference between the rates of organic carbon burial and weathering determines the long term net flux of O_2 and CO_2 to or from the sedimentary organic carbon subcycle. Because of the large kinetic isotope effect associated with photosynthetic fixation of carbon, the carbon isotopic composition of marine sediments permits an estimate of the relative importance of carbon burial in its reduced or oxidized form [Broecker, 1970; Garrels and Lerman, 1984]. The Neogene record of $\delta^{13}\text{C}$ in bulk marine carbonate (Figure 1) shows two prominent features that have been interpreted to reflect changes in global carbon cycling. An increase of $\delta^{13}\text{C}$ values from $\approx 2\text{‰}$ to $>2.5\text{‰}$ in the early to mid-Miocene is associated with the "Monterey event" of

widespread deposition of organic carbon (C_{org})-rich sediments [Vincent and Berger, 1985]. Since the mid-Miocene, bulk $\delta^{13}\text{C}$ values have declined to around 0.4‰ at present, suggesting decreasing fractional organic carbon burial [Shackleton, 1985; 1987; Kump and Garrels, 1986]. Such a decrease implies transfer of sedimentary carbon from the reduced to the oxidized reservoir by the generalized reaction



It has been estimated that enough carbon was oxidized during the late Neogene to drive an approximately 20% decrease in atmospheric O_2 content [Shackleton, 1987].

Most previous modeling studies of the Cenozoic $\delta^{13}\text{C}$ record have assumed that the magnitude of carbon isotopic fractionation associated with photosynthetic carbon fixation has remained constant with time [Shackleton, 1985; 1987; Kump and Garrels, 1986; Kaufman *et al.*, 1993; Raymo, 1994]. However, increasing evidence demonstrates that photosynthetic carbon isotopic fractionation has decreased during the Cenozoic [Arthur *et al.*, 1985; Dean *et al.*, 1986; Popp *et al.*, 1989; Freeman and Hayes, 1992]. Because isotope-based models of the carbon cycle are potentially very

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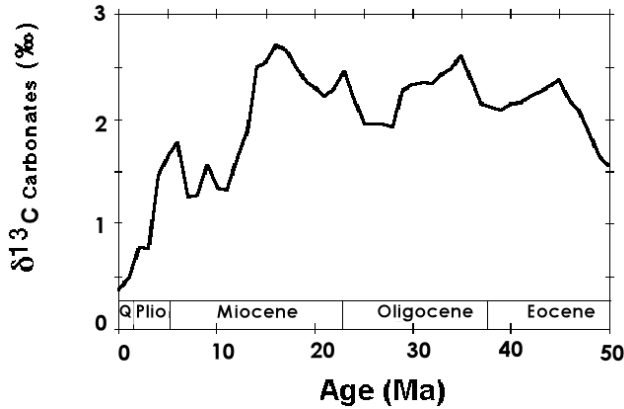


Figure 1. Late Cenozoic carbon isotopic record of bulk marine carbonate averaged in million year increments. Data from *Shackleton and Hall* [1984]

sensitive to changes in isotopic fractionation factors, a quantitative isotope model of Cenozoic carbon burial must include such information [Kump, 1989; Lasaga, 1989; Delaney and Filippelli, 1994]. Kump [1989] showed that plausible variations in carbon isotope fractionation could permit the Cenozoic $\delta^{13}\text{C}$ record to be interpreted as showing no significant change in the C_{org} burial rate and, by inference, no net change in the size of the sedimentary organic carbon reservoir. If this were true, the role of the organic carbon subcycle in setting the atmospheric budgets of oxygen and carbon dioxide would differ significantly from that proposed by Shackleton [1987]. A full evaluation of the Neogene history of sedimentary fluxes of O_2 and CO_2 must explicitly consider evidence for changes in photosynthetic C-isotope fractionation, as well as for variations in the cycling rate of the sedimentary carbon reservoirs. Below we develop a general model that includes the effects of variable isotopic fractionation factors, variable carbon fluxes from the crust, and possible variations in the isotopic composition of crustal carbon fluxes to the oceans in an attempt to better interpret the late Cenozoic sedimentary carbon isotope record.

Mass Balance for the Sedimentary Carbon Reservoir

The change in the size of the sedimentary reservoir of buried organic carbon can be written:

$$\frac{dM_{\text{org}}}{dt} = J_{\text{bur}} X_{\text{org}}^{\text{bur}} - J_{\text{er}} X_{\text{org}}^{\text{er}} \quad (2)$$

where J_{bur} and J_{er} are the burial flux and the erosional flux of total sedimentary carbon (as C_{org} + carbonate), respectively, and where $X_{\text{org}}^{\text{bur}}$ is the mass fraction of C_{org} in the carbon burial flux and $X_{\text{org}}^{\text{er}}$ is the mass fraction of C_{org} in sediments undergoing weathering. Because approximately one mole of O_2 is consumed for each mole of carbon oxidized to CO_2 , the net gain or loss of organic carbon by the sedimentary mass determines the flux of O_2 from the carbon system (if variations in volcanic degassing rates of reduced carbon species (CO , CH_4) are small enough to be ignored). The oceanic and

atmospheric reservoirs of carbon are very small relative to the sedimentary reservoirs and cannot accumulate a significant amount of carbon on a geological timescale. Therefore, for the mass of the sedimentary reservoir of total carbon to be conserved, the erosional flux of total carbon must equal the burial flux ($J_{\text{bur}} = J_{\text{er}}$):

$$\frac{dM_{\text{org}}}{dt} = J_{\text{er}} |X_{\text{org}}^{\text{bur}} - X_{\text{org}}^{\text{er}}| \equiv \frac{d\text{O}_2}{dt} \equiv -\frac{d\text{CO}_2}{dt} \quad (3)$$

where the last terms refers only to the change in O_2 and CO_2 driven by the organic carbon subcycle. Thus, the sign of the growth term for the organic carbon reservoir (dM_{org}/dt) and consequently the net flux of O_2 and CO_2 from the sedimentary carbon system does not depend simply on the burial rate of organic carbon. Rather, they depend on the difference between the fraction of C_{org} in weathered sedimentary rocks and the fraction of C_{org} in newly deposited sediments. The magnitude of this growth term is modulated by the overall rate of carbon cycling, i.e. the erosion rate for crustal carbon, J_{er} [Derry et al., 1992].

In general, $X_{\text{org}}^{\text{bur}}$ need not equal $X_{\text{org}}^{\text{er}}$. In practice, the $\delta^{13}\text{C}$ values of sedimentary carbonate can be used to constrain both terms. $X_{\text{org}}^{\text{bur}}$ represents the fraction of carbon buried in new sediments as organic matter at some time, and thus the carbon isotope mass balance is

$$X_{\text{org}}^{\text{bur}} = \frac{\delta_{\text{carb}} - \delta_{\text{riv}}}{\Delta_B} \quad (4)$$

where δ_{carb} is the isotopic composition of carbonate removed at t , δ_{riv} is the mean $\delta^{13}\text{C}$ value for carbon inputs to the oceans, and $\Delta_B = \delta_{\text{carb}} - \delta_{\text{TOC}}$ is the mean isotopic difference between carbonate and total organic carbon in sediments deposited at t [Hayes et al., 1989]. Δ_B is primarily set by the photosynthetic isotopic fractionation of primary producers but may be modified to some extent by differential preservation. For the purposes of this study, we ignore the small isotopic fractionation between seawater and carbonate. As a first approximation, we assume that δ_{riv} is given by the mean value for all sedimentary carbon, $\delta_{\text{TC}} \equiv -5\text{‰}$ [DesMarais and Moore, 1984; Holser et al., 1988]; however we consider variations in this parameter below. For the Neogene, $X_{\text{org}}^{\text{bur}}$ can be obtained from $\delta^{13}\text{C}$ data for bulk marine carbonate (Figure 1). As discussed by Shackleton [1985, 1987], for an assumption of constant isotopic composition of input into the oceans and constant isotopic fractionation (Δ_B), a -2‰ change in δ_{carb} since 15 Ma implies a significant decrease in $X_{\text{org}}^{\text{bur}}$, from approximately 0.30 to 0.22. The exact values depend on the choice of parameters, but the sense of change does not.

To obtain $X_{\text{org}}^{\text{er}}$, we need an estimate of the mean $\delta^{13}\text{C}$ value of weathered carbonate rocks through Neogene time. The mean $\delta^{13}\text{C}$ value of the sedimentary carbonate rock reservoir may be estimated as a function of time by assuming that the inputs to the carbonate reservoir are given by the Phanerozoic age curve of $\delta^{13}\text{C}$ (Figure 2) and that the outputs represent the average $\delta^{13}\text{C}$ of the carbonate rock reservoir [Derry et al., 1992]. We integrate

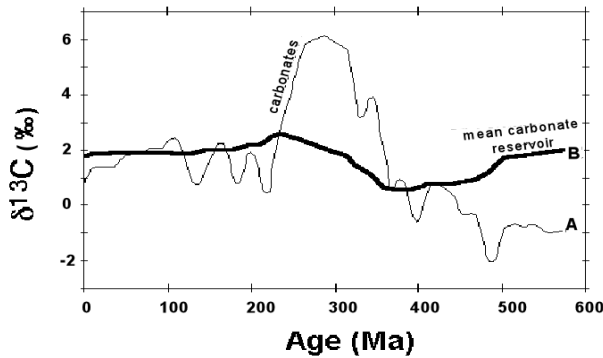


Figure 2. Curve A shows the carbon isotopic record of Phanerozoic carbonate rocks as compiled and smoothed by Lasaga [1989]. The smoothing facilitates well defined derivatives. This curve represents the instantaneous additions to the carbonate reservoir as a function of time, as newly deposited limestones. The differences between this curve and that of Shackleton and Hall [1984] for the last 50 m.y. are not significant for the purpose of calculating average reservoir values. Curve B shows the mean $\delta^{13}\text{C}$ value of the carbonate reservoir ($\delta_{\text{carb}}^{\text{ave}}$) during the Phanerozoic, calculated from (5). $\tau = 150$ Ma; initial value of 2‰ at 550 Ma is from Derry *et al.* [1992]. The long residence time of sedimentary carbonate significantly damps fluctuations in the input (curve A). We take this curve to represent the $\delta^{13}\text{C}$ value of the weathering flux (output) from the carbonate reservoir with time.

$$\frac{d\delta_{\text{carb}}^{\text{ave}}}{dt} = \frac{1}{\tau} (\delta_{\text{carb}}(t) - \delta_{\text{carb}}^{\text{ave}}) \quad (5)$$

where τ is the mean residence time of sedimentary carbonate, $\delta_{\text{carb}}(t)$ is the isotopic composition of carbonate added to the sedimentary reservoir at some instantaneous time, t , and $\delta_{\text{carb}}^{\text{ave}}$ is mean isotopic composition of the sedimentary carbonate rock reservoir (Figure 2). Variations in the input ($\delta_{\text{carb}}(t)$ values from the age curve) are strongly damped in the output ($\delta_{\text{carb}}^{\text{ave}}$) by the long (circa 150 Ma) residence time of sedimentary carbonate; thus the mean $\delta^{13}\text{C}$ value of sedimentary carbonate changes only slowly in time. For the Neogene, we estimate that $\delta_{\text{carb}}^{\text{ave}}$ is near 1.8‰. This result does not depend strongly on the choice of τ over a range of likely values (100 to 300 Ma) and not at all on the choice of initial condition. Essentially, the sedimentary carbon (organic and inorganic) reservoirs that are weathered in the Neogene are dominated by Mesozoic - lower Cenozoic sediments. Consequently, the isotopic composition of eroded carbon is similar to typical values of $\delta^{13}\text{C}$ in Mesozoic carbonates. This observation is consistent with the geologic observation that large quantities of Mesozoic-lower Cenozoic sediments have been uplifted and eroded during the late Cenozoic, as a consequence of the collisional closure of the Tethys ocean.

An independent estimate of $\delta_{\text{carb}}^{\text{ave}}$ can be obtained from observed the mass-age distribution of sediments and the isotopic age curve for carbon. Using the mass-age distribution for Phanerozoic sediments of Wold and Hay [1990] yields an estimate for $\delta_{\text{carb}}^{\text{ave}}$ during the Neogene essentially identical to

the results from Eqn. 5. An explicit calculation of the value of $\delta_{\text{carb}}^{\text{ave}}$ can also be obtained from the GEOCARB I model of Berner [1991], and the results of his model agree closely (approximately 0.1‰) with the above estimates for $\delta_{\text{carb}}^{\text{ave}}$ (R. A. Berner, personal communication, 1995). Given the excellent agreement between three independent estimates, we take 1.8 ± 0.2 as an estimate for $\delta_{\text{carb}}^{\text{ave}}$ during the Neogene.

The fraction of C_{org} in eroded carbon, $X_{\text{org}}^{\text{er}}$, can be estimated in a directly analogous fashion to the burial fraction:

$$X_{\text{org}}^{\text{er}} = \frac{\delta_{\text{carb}}^{\text{ave}} - \delta_{\text{TC}}}{\Delta_E} \quad (6)$$

where δ_{TC} is the mean isotopic composition of total sedimentary carbon ($\approx -5\text{‰}$) and Δ_E is the mean isotopic difference between the sedimentary carbonate and organic reservoirs undergoing erosion.

Isotopic Depletion of Sedimentary Organic Carbon

Evidence for a late Cenozoic decrease in the average isotopic depletion of sedimentary organic matter relative to carbonate comes from several sources. Isotopic studies of sedimentary organic matter of marine origin show that Δ_B was 5 to 7 ‰ less in the Neogene than in the Mesozoic - Paleogene [Arthur *et al.*, 1985; Dean *et al.*, 1986]. Studies of isolated porphyrins produced by marine algae show that the shift was the result of a decrease in the primary photosynthetic fractionation, and that the bulk of the change occurred after the late Eocene but before the early Miocene [Popp *et al.*, 1989; Freeman and Hayes, 1992]. Unfortunately they did not have data during this interval, which could better define the timing and rate of change. The $\delta^{13}\text{C}$ data from marine-sourced kerogens also indicate an abrupt transition to higher values in the Oligo-Miocene [Lewan, 1986]. Comparative studies of ancient and modern plant material suggest that there was no corresponding change in the depletion factor for terrestrial plants using the common C3 pathway [Hayes *et al.*, 1989]. However, C4 plants, which deplete atmospheric CO_2 by 14-20‰ less than C3 plants, appear to have become abundant during the late Miocene [Cerling *et al.*, 1993]. Consequently, beginning in the late Miocene, the mean isotopic depletion produced by terrestrial plants also decreased, in an amount proportional to the contribution of C4 plants to sedimentary carbon burial. These considerations make it clear that potential changes in the sedimentary mixing ratio between C_{org} produced by land plants and marine organisms, as well as changes in their respective isotopic compositions, must be considered in estimating Δ_B values through time [e.g., Jasper and Hayes, 1993].

There are currently no reliable direct estimates of the fraction of organic carbon buried which is derived from terrestrial sources versus marine sources. The fractions of marine and terrestrial carbon buried in marine sediments may be proportional to the net primary productivity (NPP) in each ecosystem. Recent estimates (summarized by Schlesinger [1991]) suggest that marine and terrestrial NPP are roughly equal. Organic carbon export from different terrestrial ecosystems is proportional to NPP [Kaplan and Newbold,

1993]. Using NPP as a guide, we can estimate the fraction of marine algal, C3, and C4 plant-produced carbon entering sediments during the Neogene. Combining this estimate with mean values for $\delta^{13}\text{C}$ for each source allows an estimate of the mean Δ_B as a function of time. In part because C4 plant communities are highly productive [Jones, 1992], they have become a significant contributor to C_{org} burial since circa 7 Ma, accounting for >10% of the global C_{org} burial flux despite comprising only approximately 5% of terrestrial biomass [France-Lanord and Derry, 1994]. We take the relative contributions of marine algal, C3 and C4 plant sources to the sedimentary carbon budget as 50%, 50%, and 0% before 7 Ma; and 50%, 40% and 10% afterward. Using average values of ^{13}C depletion for marine algae (-21‰), C3 (-28‰) and C4 (-12‰) plants, we obtain an average Neogene Δ_B of 24.5‰ from 25 to 7 Ma and 23.5‰ from 7 Ma to the present. This calculation demonstrates the potential importance of shifting sources of organic matter for understanding the isotopic budgets of sedimentary carbon. We estimate that Δ_E was near 28‰ for Mesozoic through Paleogene sediments [Dean *et al.*, 1986; Popp *et al.*, 1989; Freeman and Hayes, 1992; Lewan, 1986].

The available data are not sufficient to define the history of Δ_B between the late Eocene and early Miocene, so we do not present results for times prior to 25 Ma. The model results presented below for the 0-25 Ma period do not depend on the path followed Δ_B from 50 to 25 Ma. In detail, the Cenozoic evolution of carbon isotopic depletion is undoubtedly more complex than the simple history outlined here. However, the simple history we use is quite adequate for our present purpose.

Model Results: Effect of Variable Carbon Isotope Fractionation

In order to examine the impact of variable isotopic fractionation and of variable cycling rates, we show two sets of model runs in Figure 3. Curves A and B are calculated assuming a constant fractionation through time, i.e., $\Delta_B = \Delta_E = 25\text{‰}$, an assumption that has been used by many earlier authors. Although there are differences due to the effect of carbon cycling rate (discussed below) both curves show negative growth of the C_{org} reservoir after approximately 13 Ma. While the area under the curves (the integrated change) varies somewhat with the particular value chosen for the depletion factor, and with the cycling rate, the position of the crossover point from positive to negative growth (i.e., 13 Ma) does not. The qualitative behavior of the system is effectively controlled by the difference $\delta_{\text{carb}} - \delta_{\text{carb}}^{\text{ave}}$. This result is qualitatively similar to that discussed by Shackleton [1987].

Shackleton [1987] specifically considered large changes in Δ_B but ruled them out as implausible. As discussed above, evidence which has become available since the publication of his paper now demonstrates that such changes have occurred. The net change in the size of the C_{org} reservoir calculated from the isotopic mass balance is highly sensitive to changes in the mean fractionation factor. For runs C and D (Figure 3) we have used the time-dependent estimates of the fractionation factors obtained above, with $\Delta_E = 28\text{‰}$ and $\Delta_B = 24.5$ to 23.5‰. The results of runs which include variable

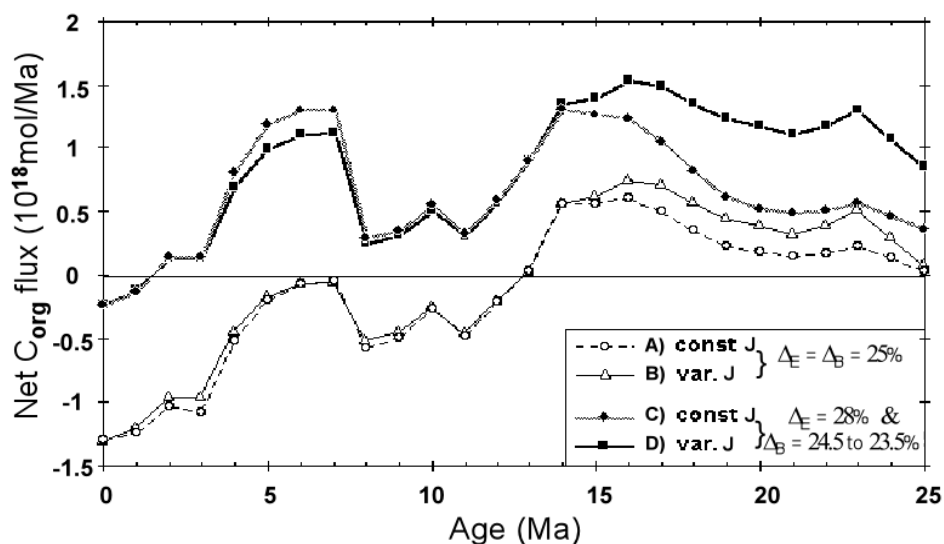


Figure 3. Net change in the size of the sedimentary reservoir of organic carbon during the Neogene (burial flux - weathering flux). The area under each curve represents the integrated O_2 flux from the organic carbon subcycle during the last 25 Ma. Open symbols indicate calculations assuming constant isotopic fractionation: $\Delta_E = \Delta_B = 25\text{‰}$. Curve A uses the present-day value of $J_{\text{er}} = 2.2 \times 10^{19}$ mol/Ma, modified from Delaney and Boyle [1988]. Curve B uses J_{er} scaled to erosion flux model of Kaufman *et al.* [1993]. In either case growth of C_{org} reservoir becomes negative near 13 Ma. Solid symbols indicate calculations with time-dependent isotopic fractionation history described in text: $\Delta_E = 28\text{‰}$, $\Delta_B = 24.5$ from 25 - 7 Ma, and 23.5 from 7 - 0 Ma. Curve C uses J_{er} fixed at present-day value. Curve D uses J_{er} scaled to erosion flux model of Kaufman *et al.* [1993]. In both cases, growth of C_{org} reservoir is positive until the Plio-Pleistocene, implying that the organic carbon subcycle is a net source for O_2 and a net sink for CO_2 during most of the Neogene.

fractionation factors are significantly different from the previous cases. Again, while the integrated change depends on the exact values chosen for the fractionation factors and the carbon cycling rate, in all cases the crossover point from positive to negative growth occurs much later. For values of Δ_B of 23 to 25‰, crossover occurs at 0 Ma to 3 Ma, respectively. Until the crossover time, the net growth of the C_{org} reservoir was positive. It is crucial to note that the absolute values are much less important than the magnitude of change, $\Delta_E - \Delta_B$, which, as argued above, is reasonably well constrained to be at least 3‰ and probably 5‰ by the late Neogene. There is some dependence on the value of δ_{carb}^{ave} as well, but values near our estimated range (1.8±0.2‰) do not significantly affect the results discussed here. For example, with $\Delta_B = 24$ ‰, changes in δ_{carb}^{ave} from 1.6 to 2.2‰ change the crossover point from 0 Ma to 3 Ma.

The results may be illustrated with the following example. Sedimentary carbonate eroded throughout the Neogene has had a $\delta^{13}C$ value near 1.8‰ (Figure 2), implying $X_{org}^{er} \approx 0.24$ for $\Delta_E = 28$ ‰. This carbon lost from the sedimentary mass was replaced with carbon deposited while $\Delta_B \approx 24$ ‰. For example, late Miocene bulk carbonate with $\delta^{13}C_{carb} = 1.5$ ‰ yields $X_{org}^{bur} \approx 0.27$, so more organic carbon was deposited at this time than was eroded. Despite falling δ_{carb} values during the late Neogene, "old" carbon eroded from the sedimentary mass was replaced by "new" carbon containing a higher fraction of organic matter (i.e., $X_{org}^{bur} > X_{org}^{er}$). Therefore, it follows from (3) that the mass of the reduced reservoir of sedimentary C_{org} increased during the late Neogene despite lower overall δ_{carb} values. Only in the Plio-Pleistocene have δ_{carb} values fallen low enough to imply zero or negative growth of the organic carbon reservoir. This result is important, and is independent of any variations in erosion (carbon cycling) rates.

An important consequence of the above results is that any calculation of the behavior of the sedimentary carbon reservoirs based on carbon isotopic abundances for the Cenozoic depends significantly on the timing of the change in Δ_B . As outlined above, it appears that the change in photosynthetic fractionation factor in the marine environment occurred between the late Eocene and early Miocene. More data on the history of photosynthetic fractionation are needed during this interval to permit a calculation of the shifts between the sedimentary carbon reservoirs through the entire Cenozoic and to remove any uncertainty about the late Oligocene and early Miocene interval.

Effect of Variable Carbon Cycling Rates

The rate of the C_{org} reservoir increase or decrease depends on the erosion/burial rate of carbon in the sedimentary system. As discussed by *Delaney and Fileppelli* [1994], several previous models have concluded that absolute C_{org} burial rates declined over the last 20 m.y. However, this apparent agreement is misleading and is largely a model-dependent consequence of holding carbon cycling rates at or near constant through time. A number of independent approaches suggest that erosion rates have increased significantly during the late Cenozoic; however, the timing and magnitude of erosion rate changes are significantly different among

different models [*Jacobsen*, 1988; *Wold and Hay*, 1990; *Richter et al.*, 1992; *Kaufman et al.*, 1993]. Therefore we present two calculations for each case of depletion factor history: one assuming a constant carbon cycling rate, and the second using the model of *Kaufman et al.* [1993] for late Cenozoic erosion rates (Figure 3). Following *Derry et al.* [1992], we scale the rate of carbon cycling in the past to the present-day exogenic flux, using the global erosion models. This approach was followed by *Kaufman et al.* [1993] and *Raymo* [1994] to estimate organic carbon burial rates during the late Cenozoic. Any significant change in carbon cycling rates will have strong impact on C_{org} burial rates. The calculated absolute rate of C_{org} burial can depend more strongly on J_{er} than on the $\delta^{13}C$ value of carbonates [*Derry et al.*, 1992]. For example, a 40% increase in global carbon erosion/burial would require a decrease in $\delta^{13}C$ of roughly 3‰ to offset the change in total C_{org} burial rates caused simply by accelerated carbon cycling. However, such a change must, by definition, have a similar impact on C_{org} weathering rates, and a significant increase in C_{org} burial rates does not necessarily imply any change in the mass balance of the sedimentary carbon reservoirs. This is an important point. An increase in erosion rate acts only as an amplifier for imbalances in the transfer of carbon between the reduced and oxidized reservoirs, which are indicated by the C-isotope mass balance (equation (3)). Here we focus on the difference between C_{org} burial and C_{org} weathering rates, which defines the rate of growth or decay of the sedimentary organic carbon reservoir. Because of the modeled Neogene increase in the erosional cycling rate of carbon, both erosion and burial rates must increase: the important question for our purposes is which does so more rapidly.

The differences in net C_{org} growth estimated with different erosion models become small with decreasing age, because all models must converge on the same present-day rate of carbon cycling (Figure 3). The differences (and uncertainties) are greatest in the early Miocene, because erosion models that use the variation of seawater $^{87}Sr/^{86}Sr$ [*Richter et al.*, 1992, *Kaufman et al.*, 1993] are sensitive to the rapid rate of change in this parameter, and to assumptions about how much of this change reflects actual changes in the weathering fluxes versus source rock changes. *Kaufman et al.* [1993] found a somewhat greater change in Miocene weathering fluxes than did *Richter et al.* [1992], followed by lower Pliocene values. The lower Pliocene values estimated by *Kaufman et al.* are in agreement with our recent recalculation of the Neogene marine Sr mass balance [*Derry and France-Lanord*, 1996], so we use their estimate here. In any case the difference resulting from a different choice of Neogene erosion rates is not large. The result with constant Δ_B and no change in carbon cycling rate (curve A, Figure 3) is similar to the calculation of *Shackleton* [1987], while the case of constant Δ_B and variable erosion (curve B) corresponds roughly to the case discussed by *Raymo* [1994], although she calculated burial only, not net change.

For a given carbon isotope depletion history, the changes in net growth of the C_{org} reservoir as a function of changing carbon cycling are relatively small (Figure 3). The primary effect is to decrease the rate of growth of the C_{org} reservoir prior to and during the early Miocene "Monterey event," because modeled erosion rates were lower at 25 Ma but climbed to

a peak near 16 Ma [Richter *et al.*, 1992; Kaufman *et al.*, 1993]. The effect of allowing Δ_B to vary in time is much more dramatic. Prior to the mid-Miocene, the rate of C_{org} growth is significantly greater when Δ_B is varied. The more realistic inclusion of variable cycling rate predicts an acceleration of growth from around 20 to 16 Ma. As carbonate $\delta^{13}C$ values fall after the "Monterey event" the difference becomes striking. The models which assume $\Delta_B = \Delta_E = \text{constant}$ show negative growth thereafter, regardless of cycling rate. However, the models with variable Δ_B show positive growth through nearly the entire Neogene. Taking the evidence for decreased isotopic fractionation into account not only affects the magnitude of growth in the calculated C_{org} reservoir but also more importantly its sign. Our calculations confirm the suggestions of Kump [1989] and Caldeira *et al.* [1993] that changing carbon isotope depletion patterns in the late Cenozoic are consistent with no net loss from the sedimentary organic carbon reservoir and, in fact, strongly suggest net growth integrated over the Neogene.

Effect of Changing $\delta^{13}C$ of Inputs to the Oceans

To this point, while allowing both carbon cycling rates and isotopic fractionation to vary, we have held the isotopic composition of the inputs to the ocean constant. However, the decrease in δ_{carb} after 15 Ma could result either from decreasing X_{org}^{out} or decreasing $\delta^{13}C$ of river inputs to the oceans [Shackleton, 1987; Delaney and Boyle, 1988; Kump, 1989]. Recent work has suggested that the latter scenario may have played a role. Osmium isotope evidence suggests that weathering of organic-rich sediments increased during the late Neogene, resulting in an increased flux of isotopically light carbon to the oceans [Ravizza, 1993; Ravizza and Esser, 1993]. To simulate this situation, δ_{riv} , representing the river flux of carbon, was allowed to decrease monotonically from -4 to -6‰ beginning at 13 Ma. For $\delta_{carb}^{ave} = 1.8‰$ this is equivalent to an increase of X_{org}^{er} from 0.24 to 0.33, because a large increase in the weathering fraction of C_{org} is necessary to drive δ_{riv} down by -2‰. These assumptions yield a Neogene history for the sedimentary carbon reservoir virtually identical to the case of constant river composition. Increased weathering of C_{org} is balanced by increased deposition required by the isotopic mass balance for a changing river isotopic input. Again, a simple example may serve to illustrate this point: for a Pliocene δ_{carb} value of +1‰, a decrease in the river input from -4 to -6‰ would imply an increase in X_{org}^{out} from around 0.25 to 0.33 (equation (2)), offsetting the increase in X_{org}^{er} almost exactly. This result supports the conclusion that the sedimentary reservoir was a net sink for organic carbon and a net source for oxygen. Regardless of the cause of falling δ_{carb} in the late Neogene (decreased fractional C_{org} burial or increased fractional C_{org} weathering), the isotopic mass balance requires that inputs to the sedimentary C_{org} reservoir exceed outputs through most of the Neogene.

Implications for Atmospheric O_2 and CO_2 During the Neogene

Using the assumptions of both constant isotopic fractionation factors and constant cycling rates previous

workers [Shackleton, 1985; 1987; Kump and Garrels, 1986] proposed that approximately 8×10^{18} moles of organic carbon were lost from the sedimentary organic carbon reservoir since the mid-Miocene, with an equal loss of atmospheric oxygen. In contrast, we find net growth of the organic carbon reservoir of 16×10^{18} moles during the same interval. As discussed above, the figure for integrated change can vary somewhat within the uncertainty of our assumptions, but the sign does not. Growth of the C_{org} reservoir implies a positive O_2 flux to the ocean-atmosphere system. Excess C_{org} burial also implies net CO_2 consumption [e.g., Arthur *et al.*, 1988]. Vincent and Berger [1985] have suggested that excess C_{org} burial during the Monterey event led to atmospheric CO_2 drawdown, which in turn contributed to mid-Miocene ocean cooling. Our results show an increase in the sedimentary C_{org} reservoir from 18-14 Ma and are thus consistent with their hypothesis. However, we find that the organic carbon cycle continued to act as a sink for CO_2 until the Plio-Pleistocene, well after the Monterey event terminated.

Enhanced chemical weathering of silicates resulting from tectonic forcing has been proposed as the dominant control for CO_2 in Neogene time [Raymo and Ruddiman, 1992], but rates of CO_2 consumption implied by this hypothesis require source of CO_2 in excess of the known volcanic sources to compensate the weathering losses [Volk, 1993]. Following the approach of Shackleton [1985, 1987], Raymo and Ruddiman [1992] and Raymo [1994] have argued that a positive CO_2 flux from the sedimentary carbon system during the Neogene could provide enough CO_2 to buffer atmospheric levels against losses by silicate weathering. Consideration of the strong evidence for variable carbon isotope fractionation does not support the notion that the organic carbon subcycle acted as a source for CO_2 during most of the Neogene. In contrast, we find that the burial of C_{org} acted as a net sink for CO_2 until the latest Neogene and thus cannot be invoked to satisfy the mass balance constraint imposed by increased silicate weathering rates (rather it compounds the problem). The growth of the C_{org} reservoir can be a significant contributor to decreasing atmospheric CO_2 during the late Cenozoic. In fact, our constraints on the magnitude of shifts between the sedimentary carbon reservoirs are currently better than those for the degassing - weathering terms for the long term CO_2 mass balance. At present the best constraint on the degassing and silicate weathering flux terms is indirect: after accounting for changes in the sedimentary carbon balance, the total net flux of CO_2 must nearly balance at all times [Rubey, 1951]. Unless there are large, unidentified sources for CO_2 in the carbon system, at least one of two hypotheses must be true in order to balance the late Cenozoic carbon budget. Either the consumption of CO_2 during weathering of continental or oceanic crust is sensitive to pCO_2 (e.g., the BLAG hypothesis [cf. Berner *et al.*, 1983; Velbel, 1993; Francois and Walker, 1992]), or the production of CO_2 by volcanism and metamorphic degassing must be very closely coupled to the weathering sink [e.g. Caldeira, 1992; Kerrick and Caldeira, 1993]. While there may be some long-term connection between weathering and subduction zone volcanic degassing or collision zone metamorphic degassing, it is unlikely that the coupling of those source terms is linked with silicate weathering rates via tectonic processes on a short enough timescale to prevent large swings in pCO_2 . Thus a direct

pCO₂ feedback on weathering rates seems essential for atmospheric stability, and the late Cenozoic does not appear to provide an exception [Folk, 1993; Caldeira et al., 1993].

Atmospheric CO₂ has a number of important sinks and sources, so any prediction about Neogene CO₂ levels in the atmosphere based on the evaluation of only one of these sinks is liable to be nonunique. In contrast, the organic carbon subcycle is the dominant mechanism determining atmospheric O₂ content during the Cenozoic. Therefore evidence for the history of pO₂ may be a better test of our predictions. Although the Neogene history of atmospheric pO₂ is not well known, we suggest that our interpretation resolves some apparent dilemmas posed by earlier models which predicted falling Neogene O₂ levels. We cite three examples of independent observations that are consistent with rising pO₂ during the late Neogene. Each observation taken independently has alternative explanations that may still be viable. However, taken together they may provide an independent assessment of the behavior of the organic carbon subcycle.

Charcoal fluxes recorded in sediments may provide one clue, as increased pO₂ should result in increased biomass burning [Watson et al., 1978]. Charcoal fluxes to North Pacific sediments increased dramatically (1 to 3 orders of magnitude) and permanently from the early Miocene to the present, an observation difficult to reconcile with predictions of a major drop in atmospheric pO₂ over the same interval [Herring, 1985]. Herring argued that the stability of elemental carbon in the geological record made it unlikely that the observed Miocene increase in charcoal flux was a preservation signal and therefore must reflect either increased wind transport or increased biomass burning. By analogy with the factors controlling eolian dust deposition [Rea, 1994], increased charcoal flux likely reflects a stronger source (i.e. more burning), not merely enhanced transport. Rea [1994] recently reviewed the history of eolian dust flux to the North Pacific and found low values until 3 to 3.5 Ma. The dust flux signal in the North Pacific is thought to primarily reflect the degree of aridity in the Asian source region [Rea, 1994]. In contrast, the increase in charcoal flux to the North Pacific in most cases is well underway by the mid-Miocene and thus significantly precedes the increase in dust flux. The data do not therefore support increased aridity as the source of the increased charcoal fluxes, at least not before the mid-Pliocene. Our calculation of Neogene O₂ fluxes from the carbon cycle is consistent with evidence for increased terrestrial biomass burning in the absence of evidence for increased aridity during this time.

The apparent radiation of C4 plants in the late Miocene [Cerling et al., 1993] may also have been influenced by rising pO₂ values. Photorespiration inhibits photosynthesis in C3 plants at high atmospheric O₂/CO₂ ratios (not simply by low pCO₂) while the C4 pathway is not affected [Edwards and Walker, 1983]. Thus rising pO₂, in combination with falling pCO₂ [Ehrlinger et al., 1991] may have conferred an advantage on C4 plants. Finally, the record of δ³⁴S in marine sulfate suggests net conversion of sedimentary sulfide to sulfate during the Neogene [Burdett et al., 1989], resulting in consumption of O₂ by the sulfur system. Although the coupling of increased sulfate burial with increased organic carbon burial is imperfect [Veizer et al., 1980; Kump, 1993],

increased Neogene sulfate burial is consistent with the results of our model. Such a coupling suggests that the sulfur cycle has responded as a negative feedback to increased oxygen produced by the carbon cycle. In fact, our model predicts the net release of 16x10¹⁸ moles of O₂ from the carbon cycle during the last 25 Ma, which is equivalent to 40% of the present atmospheric O₂ mass. Clearly negative feedback mechanisms such as increased sulfate burial are necessary to buffer atmospheric oxygen against wide swings. An estimate of Neogene O₂ consumption by sulfide-sulfate conversion based on the δ³⁴S data of Burdett et al. [1989] is about half of that produced by the carbon system. In contrast to the collective implications of the observations of increased charcoal fluxes, C4 plant radiation, and sulfur isotopic shifts, we are not aware of any independent evidence which is consistent with falling pO₂ during the Neogene. Shackleton [1987] suggested that a Neogene decrease in atmospheric pO₂ coincided with cooling deepwater temperatures, resulting in roughly conservative marine dissolved O₂ levels. While this notion is appealing, there is no a priori reason to expect such behavior. As Herbert and Sarmiento [1991] have shown, deepwater dissolved O₂ levels are quite sensitive to nutrient utilization efficiency and the sites of deepwater formation, as well as atmospheric pO₂. Given the evidence for the operation of a number of negative feedbacks on increasing pO₂, (e.g., sulfate formation, increased weathering of sedimentary kerogens, biomass burning), we estimate that the net gain of O₂ by the atmosphere probably did not exceed 20% during the Neogene and may have been less.

Causes of Neogene δ¹³C Change

The behavior of the late Neogene marine δ¹³C curve itself suggests the existence of negative feedbacks on atmospheric O₂ in addition to the sulfur cycle. Unless Δ_B decreased in exactly the same pattern as did δ_{carb} (a notion unsupported by data), the discontinuous drop of 2.5‰ in δ_{carb} since 14 Ma does imply a decrease in the relative efficiency of organic carbon burial, or an increase in the relative efficiency of organic carbon weathering. As discussed above, the net C_{org} reservoir change is mostly positive, but the rate of growth decreases as a consequence of this change in efficiency. The decrease in δ¹³C of bulk marine carbonate after 14 Ma may in part reflect decreased efficiency of the burial of organic matter in sediments in response to increased dissolved O₂ levels in the oceans. Increased dissolved O₂ could result from increased pO₂, cooling oceanic deepwater temperatures [Shackleton, 1987], or shifting the sites of deepwater formation to high latitude regions where nutrient utilization is inefficient [Herbert and Sarmiento, 1991].

Increased weathering efficiency of organic-rich sediments is an alternative explanation. Ravizza [1993] and Ravizza and Esser [1993] suggest that Neogene marine Os and C isotope records could reflect increased weathering of old black shales beginning in the mid-Miocene. If the fall in δ_{carb} is caused by lower δ_{riv}, this would imply increased fractional weathering of organic carbon rich sediments (i.e., X_{org}^{er}). A simple increase in total carbon weathering will change the river C flux but not its isotopic ratio. However, to drive a 2‰ decrease in δ_{carb}, the rate of C_{org} weathering must increase substantially relative

to the rate of carbonate weathering, by roughly 40%. Tectonic unroofing and weathering of organic carbon-rich shales may have increased more rapidly than for carbonates over the last 14 m.y., but given that shales and carbonates are usually interbedded in typical sedimentary sections, it may not be reasonable to have such large, long-term changes in the relative rates of organic-rich shale versus carbonate weathering driven by tectonics. If oxidative weathering rates of sedimentary C_{org} depend positively on pO_2 , our model would predict enhanced C_{org} weathering as a consequence of atmospheric change. The nature of a $pO_2 - C_{org}$ weathering rate feedback is unknown, although it is probably nonlinear and weak in the pO_2 range under discussion (given that most C_{org} eroded today is oxidized [Holland, 1978]), an increase in pO_2 cannot increase the total oxidation rate much). As noted above, other feedbacks involving the sulfur cycle and biomass burning were probably significant, and limited O_2 increases. Thus we suspect that the apparent agreement between the magnitude of the Neogene integrated O_2 flux from the organic carbon subcycle and the 40% increase in C_{org} weathering rates required to drive all of the δ_{carb} change is fortuitous. In our opinion it is unlikely that change in the relative weathering rate of sedimentary organic matter is the primary driver for Neogene variations in δ_{carb} , but the question remains open. Tectonic control on weathering rates and any pO_2 feedback control are not exclusive of one another, and it is possible that both play a role.

Conclusions

We developed an isotopic mass balance model for the Neogene evolution of the sedimentary organic carbon reservoir, allowing for variations in photosynthetic fractionation factors, carbon cycling rates, and the isotopic composition of riverine carbon. As additional inputs to this model we use the available constraints on ^{13}C depletion during the Cenozoic, as well as estimates of rates of sedimentary carbon cycling. This study points out the impact that the evidence for changing carbon isotopic fractionation factors during Cenozoic time has for interpreting the $\delta^{13}C$ record of marine carbonates. An apparently robust result is that growth of the C_{org} reservoir was positive through most of the Neogene, until the Plio-Pleistocene. This result has significantly different implications for atmospheric history than models using constant isotopic fractionation. In particular, we find that the organic carbon subcycle acted as a source for atmospheric oxygen during the Neogene and a sink for atmospheric CO_2 . The Neogene budgets for the sedimentary carbon reservoirs are presently better constrained than the degassing-silicate weathering budgets and indicate that the growth of the organic carbon reservoir can contribute significantly to late Cenozoic atmospheric change. Finally, our assessment of the sedimentary carbon isotope mass balance indicates that, in general, satisfactory models of carbon cycling and atmospheric evolution require more detailed knowledge of isotopic depletion factors as a function of time. It thus highlights the need for better data on the relative contributions of marine and terrestrial biomass to the sedimentary carbon record, carbon isotope depletion in each of those environments, and absolute carbon cycling rates, in order to refine isotope-based models of the carbon cycle.

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