



Closing the geologic carbon cycle

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Estimates of sedimentary organic carbon burial fluxes based on inventory and isotope mass balance methods have been divergent. A new calculation of the isotope mass balance using a revised assessment of the inputs to the ocean-atmosphere system resolves the apparent discrepancy. Inputs include weathering of carbonate and old kerogen, geogenic methane oxidation, and volcanic and metamorphic degassing. Volcanic and metamorphic degassing comprise $\approx 23\%$ of the total C input. Inputs from isotopically light OC_{petro} and CH_{4-geo} drive the mean $\delta^{13}C$ of the input to $-8.0 \pm 1.9\%$, notably lower than the commonly assumed volcanic degassing value. The isotope mass balance model yields a modern burial flux $= 15.9 \pm 6.6 \text{ Tmol y}^{-1}$. The impact of the mid-Miocene Climatic Optimum isotope anomaly is an integrated excess deposition $\approx 4.3 \times 10^6 \text{ Tmol}$ between 18 and 11 Ma, which is both longer and larger than estimates for the total degassing by the Columbia River Basalt eruptions, implying a complex carbon system response to large eruptive events. Monte Carlo evaluation finds that late Cenozoic net growth of the carbonate reservoir is very likely while net growth of the C_{org} reservoir is less certain but more likely than not. At present, subduction does not appear to keep up with net sedimentation and the overall masses of sedimentary carbonate and organic carbon are likely increasing. Growth in the sedimentary C_{org} reservoir implies oxidation of the surface environment and likely increases in atmospheric pO_2 .

carbon cycle | weathering | carbon burial

The sedimentary reservoirs of carbonate and organic carbon integrate the processes of weathering and sedimentation, and degassing and subduction over time. The fluxes into and out of these reservoirs are linked to climate and the redox state of the Earth surface environment. The major fluxes in the long-term exogenic carbon cycle include volcanic and metamorphic degassing of CO_2 , carbonate and silicate weathering, carbonate sedimentation, carbonate addition to the altered oceanic crust (AOC), and subduction (1). For the organic carbon subcycle, they include burial of organic carbon in sediments, erosion, and oxidation of organic carbon from old sediments, the generation and oxidation of geogenic methane, and subduction (2).

Weathering of rocks consumes atmospheric and soil acidity which is itself largely a product of the reaction of carbon dioxide and water. Weathering reactions generate alkalinity which is removed by carbonate precipitation in the oceans, thus buffering the pH of the surface environment and removing carbon dioxide from the ocean-atmosphere system, a process that is a major long-term regulator of planetary climate (1, 3). Consequently, the accumulation of carbonate sediment contains a record of both the degassing history of the Earth and the buffering reactions that have stabilized the Earth's climate within the field of liquid water stability through nearly all of Earth history. Concurrently, photosynthetic production of organic carbon consumes CO_2 , and a small fraction of net primary production is buried in sediments for geologic time scales. The burial of organic carbon also removes CO_2 from the ocean-atmosphere system at a rate that is broadly similar to chemical weathering (4), while oxidative weathering of old organic carbon-bearing sediments returns CO_2 (5). These long-term fluxes are small compared to annual net primary production and respiration, but over time scales of 10^5 y and longer can also play an important role in regulating the Earth's climate. Additionally, the generation of a large reservoir of reduced carbon is a key part of the planetary redox budget. Di-oxygen produced by photosynthesis, sulfate, and ferric iron can accumulate in the surface environment when the corresponding fraction of reduced organic matter is sequestered in sediments or subducted to the mantle. The growth of the sedimentary organic carbon reservoir over time plays a fundamental role in the long-term oxidation of the Earth's surface environment (6). Information on how the sedimentary reservoirs of carbon and organic carbon have changed over time is therefore essential for understanding the evolution of the Earth's surface environment including climate and atmospheric oxygen.

Significance

Sedimentary organic carbon burial is an important process influencing the global carbon, sulfur, and oxygen cycles, but this flux is not well known. I present a new analysis of the carbon stable isotope mass balance explicitly accounting for recycling of sedimentary carbonate and kerogen that permits an improved estimate of the global flux since 35 Ma. The analysis resolves large previous differences between inventory- and isotope-based estimates. The flux of geogenic methane is shown to be important given its redox state and isotopic composition. Both the sedimentary carbonate and organic carbon reservoirs appear to be growing even accounting for losses to subduction. The growth of the organic carbon reservoir implies oxidation of the surface environment and likely increasing pO_2 .

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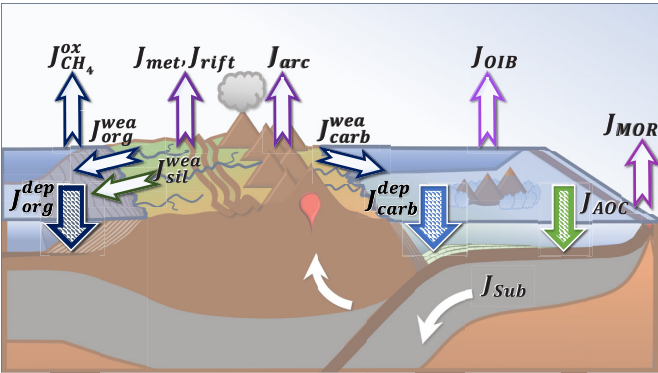


Fig. 1. Schematic illustration of input and output fluxes to and from the sedimentary carbon reservoirs. Weathering fluxes (carbonates, silicates, oxidation of old organic carbon and of geogenic methane) and degassing from volcanic (arcs, OIB, MOR, and continental rift settings) and metamorphic sources deliver C to ocean-atmosphere system from the crust and mantle. Deposition of sedimentary carbonate and organic carbon and alteration of the oceanic crust remove it. Subduction returns C to the crust-mantle system. Symbols are listed in Table 1.

Erosion and weathering destroy old sediments at the same time as they produce new ones; this shifts the mean age of sediments although it does not change the overall sedimentary (or meta-sedimentary) mass. However, subduction returns sediment including carbon to the mantle; over time subduction limits the growth of the sedimentary carbon mass (7). Developing a complete carbon cycle has been an elusive goal because important fluxes between the various Earth reservoirs can be difficult to constrain quantitatively, and various fluxes can have different characteristic time scales. Further, while steady state assumptions can be helpful in constraining budget terms for some reservoirs and processes there is no requirement for steady state in the sedimentary carbon reservoirs even at multimillion year time scales. Here, I reassess geologic carbon cycle fluxes for inorganic and organic carbon while reconciling some long-standing discrepancies between inventory vs. isotope mass balance approaches to resolving organic carbon fluxes. I consider both the sedimentary cycles of erosion/weathering and deposition and the impact of subduction of carbon-bearing sediments. The available data and constraints indicate non-steady-state behavior for the sedimentary carbonate and organic carbon reservoirs; however, important pathways in the long-term carbon cycle remain insufficiently constrained to address some questions with confidence.

Carbon Fluxes in the Sedimentary Cycle

The major fluxes in the long-term carbon cycle are illustrated in Fig. 1. A fundamental challenge is that establishing the net function of the carbon cycle is a question of assessing relatively small differences between uncertain fluxes. Such small differences integrated over geologic time can result in important changes in carbon reservoirs and the global surface redox state, but it is difficult to resolve such changes with confidence. Both reservoir inventory (mass) estimates and isotopic mass balance approaches are useful tools.

For the carbonate system, the weathering fluxes of carbonate and silicate rocks are reasonably well constrained by studies of river geochemistry. Carbonate weathering fluxes are 12 to 13 Tmol y^{-1} (8) (Table 1). Global carbonate sedimentation fluxes have been estimated in many studies, but recent work has largely settled on a range of 24 to 31 Tmol y^{-1} (9–14), which includes 2 to 3 Tmol y^{-1} of detrital carbonate (15). Multiple studies conclude that carbonate accumulation rates in marine sediments have increased

Table 1. Estimates of recent carbon fluxes and mean isotopic compositions into and out of coupled ocean-atmosphere system

	symbol	flux, Tmol y^{-1}	\pm	$\delta^{13}C$, ‰	\pm
Input terms					
Carbonate weathering	J_{carb}^{wea}	12.3	3.7	1.8	0.3
OCpetro oxidation	J_{org}^{wea}	8.1	2.2	−22	2
CH ₄ -geo oxidation	$J_{CH_4}^{ox}$	2.0	1.2	−44	2
MORB volcanism	J_{MOR}	1.3	0.8	−5.5	1
OIB volcanism	J_{OIB}	1.3	1.0	−6	1.5
Arc volcanism	J_{arc}	4.5	1.5	−3.1	0.3
Rift degassing	J_{rift}	4.2	3.3	−5	2
Metamorphic degassing	J_{met}	3.0	2.0	1.5	1.5
Silicate weathering	J_{sil}^{wea}	11.9	2.1		
$\Sigma inputs$		48.6	6.3	−8.0	1.9
Output terms					
Carbonate sedimentation	J_{carb}^{bur}	25.7	4		
C _{org} burial (inventory)		(13.3)	(6.7)		
C _{org} burial (isotope)	J_{org}^{bur}	15.9	6.6		
AOC carb	J_{AOC}^{carb}	0.7	0.5		
AOC org	J_{AOC}^{org}	0.15	0.1		
$\Sigma outputs$		42.4	7.8		
Subduction terms					
Carbonate subduction	J_{sub}^{carb}	5.0	2		
C _{org} subduction	J_{sub}^{org}	1.25	0.4		
$\Sigma subduction$		6.25	2		

Uncertainties are given as $\pm 1\sigma$. Summed fluxes obtained from Monte Carlo simulation of may differ slightly from simple sums. A complete set of sources for the data used to compile this table and additional notes are given in [SI Appendix, Table S1](#).

significantly over the late Cenozoic, although calibration differences result in a range of absolute magnitudes (11, 13, 16–21). A smaller flux of carbonate is removed by reaction to form AOC. The AOC flux is currently estimated as <1 Tmol y^{-1} but is believed to have been higher in the past (22). Carbonate sedimentation exceeds carbonate weathering by approximately the silicate weathering flux, which consumes 11 to 12 Tmol C y^{-1} (8, 23). Thus, deposition of new carbonate is currently nearly double the rate for the weathering of old sedimentary carbonate, as originally proposed in the BLAG model (1).

The organic carbon subcycle has been less easy to characterize (24). Organic carbon fluxes include the oxidation of old sedimentary carbon (OC_{petro}), the oxidation of geogenic methane, and the deposition of organic carbon-bearing sediments. The oxidative weathering of OC_{petro} has recently been estimated from associated rhenium fluxes (5). The detrital flux of OC_{petro} (not oxidized) to the oceans is estimated to be ≈ 3.6 Tmol y^{-1} (25). A fraction of this carbon in marine sediments is oxidized in diagenetic reactions while the rest is reburied in new sediments. The preservation efficiency for detrital C_{org} has been estimated to be 0.20 to 0.44 (26), implying an additional oxidation flux of 2.0 to 2.9 Tmol y^{-1} , albeit with considerable uncertainty. The generation of basin gas (geogenic methane) and its oxidation is a potentially important flux because of its high oxidative O_2 consumption and low $\delta^{13}C$ value. Estimates for geogenic methane flux (CH_{4-geo}) vary widely. Etiope and Schweitzer (27) and Nicewonger et al. (28) estimate $3.75 \pm$

1.5 Tmol y^{-1} , while (29) propose much lower values (<0.5 Tmol y^{-1}) based on the ^{14}C content of ice core CH_4 . The differences in estimates of the CH_{4-geo} fluxes are large and potentially significant for both the overall C budgets and the global redox budget.

A sediment inventory approach was used by ref. 30 to estimate the organic carbon (C_{org}) burial flux, who found that high sedimentation regions dominated C_{org} burial. The most widely cited estimate for C_{org} burial is from ref. 4 who recalculated Berner's data with a larger area of high sedimentation rate deposition, resulting in an increased estimate of C_{org} burial = 13.3 Tmol y^{-1} without defining uncertainties (Berner gave the uncertainty of his original estimate to be approximately $\pm 50\%$). Yet the basic data behind this calculation has not been substantially revisited since Berner's work over 40 y ago. A recent estimate based on ODP core data found Plio-Pleistocene values of 12.5 to 19.2 Tmol y^{-1} (31), but the number of cores with records for any given interval is small and there are no data for sites shallower than 500 m water depth.

Other estimates come from biogeochemical models. Muller-Karger et al. (32) calculated a modern C_{org} burial flux = 12.5 Tmol y^{-1} but this did not include any terrestrial input and excluded coastal areas with <50 m water depth and so is a minimum. Dunne et al. (33) obtained much higher values (65 ± 30 Tmol y^{-1}); they attributed the higher value in part to inclusion of shallow water sediments. Such high values would create very large imbalances in the long-term carbon budget and very likely do not represent long-term additions to the sedimentary mass.

Isotopic Mass Balance. The sedimentary carbon isotope budget can be used to quantify the mass of organic carbon in global sediments. The mass fraction of C_{org} added to marine sediments for a given interval is:

$$f_{org} = \frac{J_{bur}^{org}}{J_{bur}^{org} + J_{bur}^{carb}} = \frac{\delta_{carb} - \delta_{in}}{\delta_{carb} - \delta_{org}}, \quad [1]$$

where J_{bur}^{org} and J_{bur}^{carb} are the depositional flux of organic and carbonate carbon, $\delta_{carb} = \delta^{13}C$ of carbonate deposition, δ_{org} is the $\delta^{13}C$ of C_{org} deposition, and δ_{in} is the mean isotopic composition of inputs to the ocean (SI Appendix). While δ_{carb} and δ_{org} can in principle be estimated by measuring a representative sample of sediments, biases in preservation and sampling and diagenesis can be confounding factors. Kump (34) showed that it is the ocean surface carbon reservoir that drives the isotopic mass balance. The difficulties include that platform carbonates are rather susceptible to diagenesis while planktonic foraminifera (for example) may live partly in the thermocline and thus inherit a mixed shallow-deep $\delta^{13}C$ signal, there are species-specific fractionations, and there are significant horizontal and vertical gradients in the $\delta^{13}C$ of dissolved inorganic carbon in the oceans. It is difficult to assess the overall reliability and potential bias of the shallow records (35). Consequently, I take the densely sampled and astronomically tuned CENOGRID benthic record (36) as broadly representative of the $\delta^{13}C$ variations of the Cenozoic oceans (Fig. 2A). The benthic signal is offset to low $\delta^{13}C$ values relative to coeval bulk carbonate and planktic data but in most cases changes in $\delta^{13}C$ in both shallow and deep archives appear to mirror one another, implying the benthic records capture variability in the long-term carbon isotope record. The offset between bulk and benthic records varies with time and location and the strength of the biological pump, here I assume that the mean offset is $0.9 \pm 0.2\%$. The organic carbon dataset is that compiled by Hayes et al. (37) (Fig. 2B). Obtaining δ_{in} is less straightforward. δ_{in} is commonly

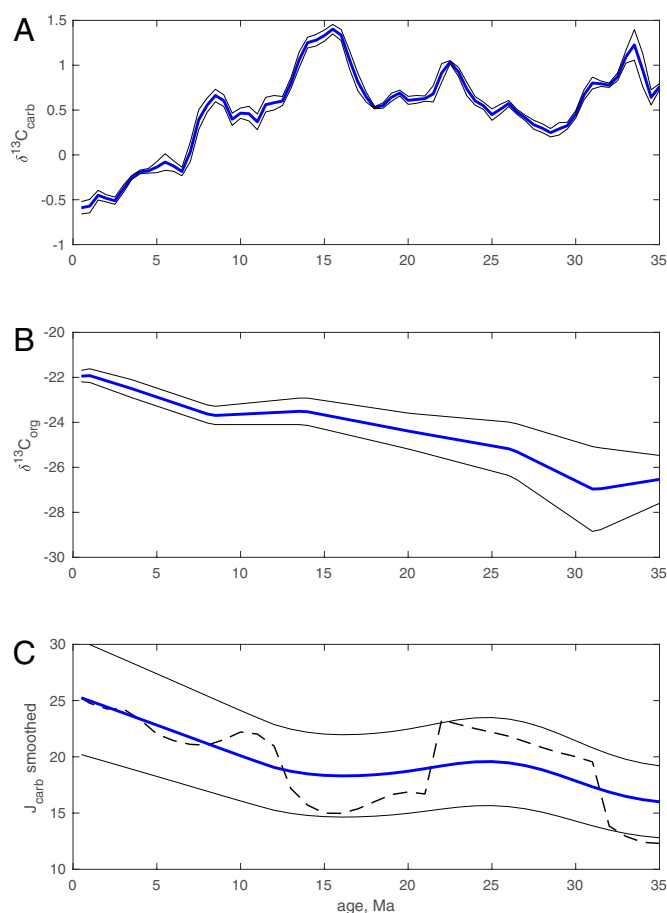


Fig. 2. Late Cenozoic marine sediment isotopic compositions and carbonate deposition fluxes. (A) $\delta_{carb}^{13}C$ (blue line) from CENOGRID (36) using 500 pt running mean with 1σ uncertainty (black lines). (B) $\delta_{org}^{13}C$ (blue line) from (37) with 1σ uncertainty (black lines). (C) Smoothed late Cenozoic carbonate sedimentation $J_{carb}^{13}C$ (blue line) from ref. 13 with 1σ uncertainty (black lines). Unsmoothed estimates are indicated by the dashed black line.

taken to be close to the value of volcanic degassing inputs. There are differences between the isotopic composition of CO_2 from the mid-ocean ridges (MORs) and arcs, but the mean $\delta^{13}C$ of volcanic degassing has been estimated to be in the range -4.6 to -3.8% (38). This range plus the late Cenozoic data for the $\delta^{13}C$ of the sedimentary outputs yields estimates of $f_{org} \approx 0.14$ to 0.25 . A modern carbonate sedimentation flux of 26 Tmol y^{-1} therefore implies a modern C_{org} burial flux ≈ 4.5 to 8.5 Tmol y^{-1} (e.g., refs. 37 and 39), notably less than the inventory estimate. Yet the value of δ_{in} need not be equal to the degassing value because it represents an average of time-variable inputs from sedimentary sources as well as different degassing sources (40, 41). Among the important input terms are the oxidation of OC_{petro} and CH_{4-geo} . Data from river sediments [MOREPOC, (42)] provides a constraint on the $\delta^{13}C$ of OC_{petro} in the weathering environment (Fig. 3). Excluding values that are potentially impacted by bomb ^{14}C , the data show a strong relationship between ^{14}C content (as Fm or “fraction modern”) and $\delta^{13}C_{org}$. The OC_{petro} value estimated for ^{14}C -free samples is $\approx -21.6\%$, similar to that obtained from a smaller dataset from the Southern Alps, NZ (-21.2% , (43)). The value obtained is distinctly heavier than the mean $\delta_{org}^{13}C$ of Phanerozoic sediments [$-27.3 \pm 2.0\%$, (37)]. Processes of diagenesis and catagenesis are likely responsible for the loss of isotopically depleted C. The evolution of kerogen with thermal maturation is toward lower H/C ratios by generation of CH_4 (44). Geogenic gas has $\delta^{13}C =$

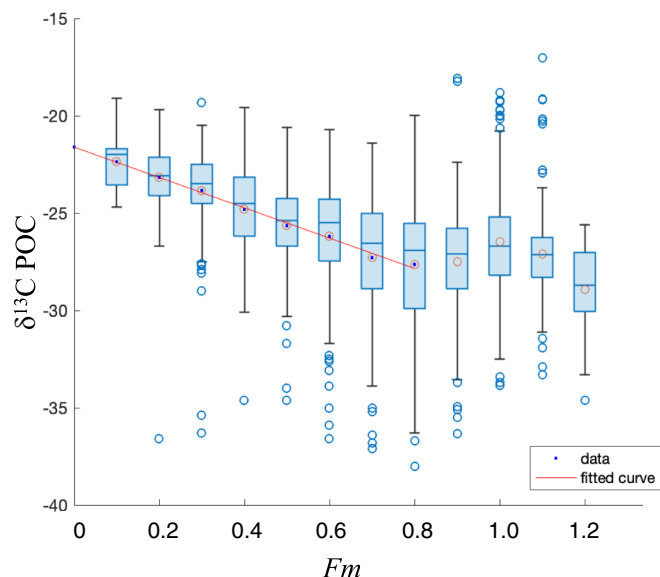


Fig. 3. Radiocarbon content (fraction modern = F_m) of river particulate organic carbon vs. $\delta^{13}\text{C}$ from MOREPOC database, $n = 2,158$ (42). Data were plotted in bins of $F_m = 0.1$. Circles are mean values, center lines are medians, boxes are 25 to 75% quantiles, whiskers are the 1.5 interquartile range (IQR), outliers are data outside 1.5 IQR. The fit is to the mean values with $F_m \leq 0.8$ (slope = -6.96 ± 0.96 , 1 SE), intercept = -21.6 ± 0.3 , $r^2 = 0.99$). This avoids apparent contamination from bomb radiocarbon which appears to affect the data at higher F_m . Similar results for the radiocarbon-free end member are obtained for different data limits and without binning (SI Appendix, Fig. S1).

$-44 \pm 2\text{‰}$ (45) so residual kerogen that has undergone catagenesis to generate methane will be correspondingly enriched in ^{13}C . Using the flux and isotopic values in Table 1 the isotopic balance between the ^{14}C -free river sediment fraction (OC_{petro}) and $CH_{4\text{-geo}}$ is approximately:

$$\delta^{13}\text{C}_{\text{ker}} = \frac{J_{OC_{\text{petro}}} \delta_{OC_{\text{petro}}} + J_{CH_4} \delta_{CH_4}}{J_{OC_{\text{petro}}} + J_{CH_4}} = -26.4 \pm 0.8\text{‰}. \quad [2]$$

The estimated kerogen value is quite close to the average δ_{org} in Phanerozoic sediments, indicating that the isotopic enrichment observed in the MOREPOC river sediment data is compatible with the loss of isotopically depleted methane during catagenesis, although other processes undoubtedly contribute to the shift in $\delta^{13}\text{C}$ of old mature and weathered kerogens. Regardless of the details of the processes that shift OC_{petro} to heavier $\delta^{13}\text{C}$ values, the heavy OC_{petro} values influence the mean input to the oceans from recycled sedimentary organic carbon.

Other sources of input to the oceans include volcanic degassing, rift and metamorphic degassing from continental interiors, and reverse weathering reactions (Fig. 4 and Table 1). Here, the MOR and ocean island basalt (OIB) CO_2 fluxes are estimated from recent studies of melt inclusions (Table 1). Rift and arc-related degassing fluxes are more difficult to constrain since they include noneruptive and diffuse fluxes (46, 47). While it is commonly assumed that volcanic degassing is the major input of CO_2 , the estimate of MOR, OIB, arc, and rift-related inputs here is ca. 1.1 Tmol y^{-1} (with a mean $\delta^{13}\text{C}_{\text{volc}} \approx -4.2\text{‰}$), about 23% of the total inputs. An additional but not well-constrained flux from decarbonation reactions (metamorphic degassing) is ≈ 2 to 4 Tmol y^{-1} from both collisional orogens (48) and arcs (49); the decarbonation flux is isotopically heavier than the volcanic fluxes (48). Total degassing fluxes on this order are necessary to balance the currently observed silicate weathering flux on land and on the seafloor while

maintaining near-constant ocean-atmosphere CO_2 since at least the early Miocene (21). Coogan and Gillis (50) used the oxygen isotope mass balance between the sink for ^{18}O during secondary mineral formation and its supply from MOR hydrothermal systems to argue that the long-term degassing flux has been $\approx 3.4 \pm 1.8 \text{ Tmol y}^{-1}$. They suggest that the current high rates of silicate weathering in turn require high rates of degassing that may not be typical of the longer-term Phanerozoic average. However, at least for the recent past, it is difficult to reconcile their lower estimate with observations from known volcanic sources and the silicate weathering flux. The discrepancy between different methods used to estimate CO_2 degassing poses important questions for our understanding of how to best constrain this flux and how it may have changed over time.

The flux-weighted mean isotopic input to the oceans is

$$\delta_{\text{in}} = \frac{\sum J_i \delta_i}{\sum J_i}, \quad [3]$$

where J_i are the input fluxes and δ_i are their isotopic compositions (Fig. 4). A Monte Carlo calculation combining the various inputs and their uncertainties (from Table 1; see SI Appendix for details of calculation) yields a mean $\delta_{\text{in}} = -8.0 \pm 1.9\text{‰}$, substantially more negative than estimates of volcanic sources and consistent with significant contributions from OC_{petro} oxidation and CH_4 oxidation in the isotopic budget. It is important to note that some of the terms in the CO_2 budget are not well known, nor are their uncertainties, so this estimate must be regarded as provisional.

To obtain the organic carbon burial flux (Eq. 1) can be restated as

$$J_{\text{bur}}^{\text{org}} = J_{\text{bur}}^{\text{carb}} \left(\frac{\delta_{\text{carb}} - \delta_{\text{in}}}{-\delta_{\text{org}} + \delta_{\text{in}}} \right), \quad [4]$$

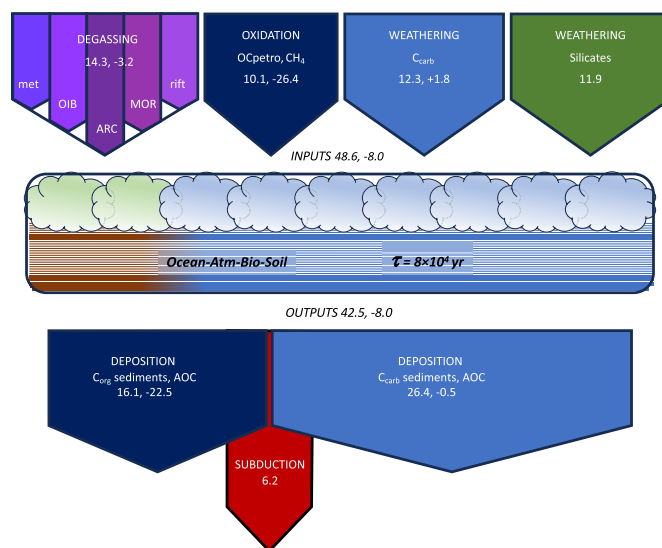


Fig. 4. Schematic illustration of carbon fluxes (Tmol y^{-1}) and their isotopic compositions ($\delta^{13}\text{C}$, italic) into and from the active ocean-atmosphere-biosphere-soil system. Silicate weathering is not assigned a unique $\delta^{13}\text{C}$ value since it draws CO_2 from the active reservoirs, not directly from a mantle or crustal source. The major inputs (degassing, oxidative weathering, carbonate weathering, and silicate weathering) have broadly similar mass fluxes. Carbon has a residence time in the active reservoirs of $\approx 8 \times 10^4 \text{ y}$ so the time scale to reach steady state in this subsystem is $\leq 0.4 \text{ Ma}$. Outputs are sedimentary deposition and addition to AOC. The input-output subduction fluxes here (Table 1) sum to near zero but that constraint was not imposed. The much longer residence time of C in sediments does not require steady state for those reservoirs even at 10^7 y time scales.

permitting calculation of the organic carbon burial rate as a function of the carbonate burial rate and the isotopic mass balance. Here I use the carbonate burial rate data through the late Cenozoic from ref. 13, as these authors provide both estimates and uncertainties for the interval of interest and give a modern value for $J_{bur}^{carb} = 25.7 \text{ Tmol yr}^{-1}$. Because the focus here is the longer-term variation in carbon fluxes I use a smoothed version of the J_{bur}^{carb} data (Fig. 2). Using the above estimate of δ_{in} , a Monte Carlo evaluation of Eq. 3 using the data in Table 1 yields a modern C_{org} burial rate of $15.9 \pm 6.6 \text{ Tmol yr}^{-1}$, similar to the inventory-based estimates (Fig. 4). This is a substantial increase of J_{bur}^{org} relative to previous isotope-based estimates that relied on volcanic degassing values for δ_{in} (e.g., refs. 37 and 39). While the new agreement between the isotope and inventory methods is encouraging both estimates continue to have significant uncertainties.

Discussion

The isotope-based estimate of J_{bur}^{org} permits calculation through time with the caveat that past input fluxes and/or their isotopic compositions could have varied. Fig. 4 presents an estimate since 35 Ma, likely a short-enough time interval that input variations should fall within the uncertainty envelope in Table 1. The burial flux of organic carbon increases substantially from the Oligocene to present, roughly following the increasing carbonate sedimentation but modulated by fluctuations in the $\delta^{13}\text{C}$ mass balance. Modern fluxes show an imbalance between the oxidation fluxes of old carbon (OC_{petro} and CH_{4-geo}) and the burial of new C_{org} . As with carbonate carbon, a larger flux of C_{org} is accumulating in marine sediments than is being oxidatively recycled from old sediments, although this apparent imbalance lies within the uncertainty envelope. A potential imbalance between sedimentary C_{org} oxidation and burial has implications for the global redox balance but calculations of the oxidation fluxes of OC_{petro} and CH_{4-geo} must consider the oxidative demand for each. The O_2/C ratio for oxidation of mature kerogen (Type III/IV with low H/C and O/C ratios) is ≈ 1.2 while for CH_4 the O_2/C for oxidation = 2. Taken together the O_2 demand of OC_{petro} and $CH_{4-geo} \approx 13.7 \text{ Tmol yr}^{-1}$, within uncertainty of the C_{org} burial fluxes by either the inventory or isotope mass balance method. Oxidation of CH_{4-geo} accounts for $\approx 30\%$ of the total O_2 demand, demonstrating the potential leverage of methane fluxes on the redox balance, yet as stated above estimates of geogenic methane flux vary widely. I note that the redox budget cannot readily be closed using proposed small CH_{4-geo} fluxes that are based on the ^{14}C content of ice core CH_4 (29) but it is important to keep in mind the difference between the geologic time scales addressed here and the short time scale associated with the ^{14}C -based estimates.

The model results for J_{bur}^{org} are only modestly sensitive to shorter-term variations in δ_{carb} . As a test, I eliminated the positive δ_{carb} anomaly between 20 and 10 Ma associated with the Miocene Climatic Optimum (MCO). The resulting difference in J_{bur}^{org} is given in Fig. 5, indicating that the MCO is associated with an integrated anomalous C_{org} burial flux of ca. $4.3 \times 10^6 \text{ Tmol}$ from 11 to 18 Ma. The anomalous C_{org} burial associated with the MCO is an order of magnitude larger than CO_2 outgassing associated with the Columbia River Basalt (CRB) eruptions [$4.1 \pm 0.7 \times 10^5 \text{ mol}$; (51)] and continues well past the main CRB activity phase. This behavior implies a complex carbon system response to the CRB events, and perhaps to other large eruptive events (Fig. 6).

The implied imbalance between carbon weathering and deposition remains a challenging calculation given that we must sum

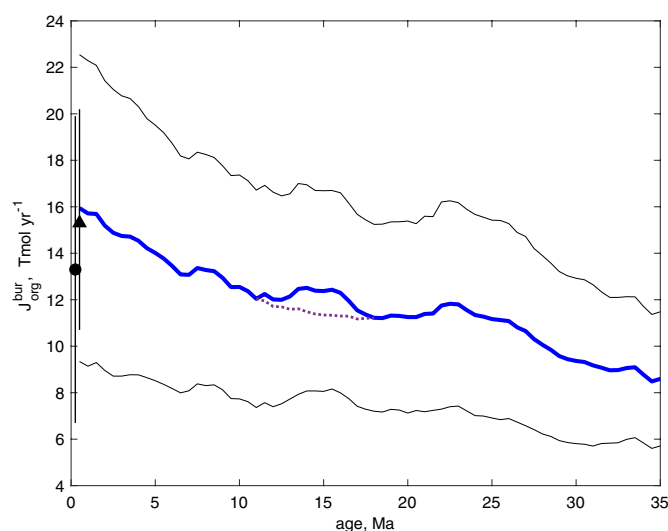


Fig. 5. Late Cenozoic organic carbon burial flux (Tmol yr^{-1}) obtained from isotope mass balance model (bold blue line; black lines $\pm 1\sigma$). The dashed line represents results when the positive $\delta^{13}\text{C}_{carb}$ anomaly associated with the MCO is arbitrarily removed. The black circle indicates inventory-based estimate from ref. 4 the triangle is Plio-Pleistocene ODP-based estimate from ref. 31. Black bars are uncertainties of the inventory-based estimates.

a set of uncertain terms. CO_2 fluxes from intracontinental rifts and metamorphic decarbonation in orogenic and arc regions are not well sampled (46). There are few data-driven estimates of the metamorphic CO_2 flux. Evans et al. (48) obtained values of CO_2 degassing for 150 km of strike length along the Himalayan front that are similar per unit length ($8.8 \times 10^7 \text{ mol C km}^{-2} \text{ yr}^{-1}$) to many volcanic arc systems (52), but the region they sampled is small fraction of all orogenic regions that produce CO_2 . Nonvolcanic degassing of carbon remains poorly known; one global estimate is around 7 Tmol yr^{-1} but is admittedly not well constrained (53). The maintenance of high sulfide-related carbonate dissolution fluxes from active orogens could also be an important CO_2 source (54). Burke et al. (55) obtained a global pyrite oxidation flux of 1.3 Tmol yr^{-1} ; if all sulfuric acid generated by sulfide oxidation was neutralized by carbonate dissolution, it would imply a CO_2 flux of the same magnitude; consequently, this value is an upper bound. This bound is $\leq 10\%$ of total carbonate weathering and is not significantly different from that obtained by ref. 56. Recent data on intraplate volcanism suggests that while ocean island basanites produce less magma than MOR tholeiites their CO_2 contents are much higher and so they may contribute a similar CO_2 flux (57); the global CO_2 flux from OIB remains inadequately characterized.

The net fluxes of C to the oceans from volcanic and metamorphic degassing, oxidative consumption of both OC_{petro} and CH_{4-geo} , and carbonate weathering are $36.6 \pm 5.9 \text{ Tmol yr}^{-1}$. Carbonate and organic sedimentation and AOC fluxes are $42.4 \pm 7.8 \text{ Tmol yr}^{-1}$, which is slightly larger than but within uncertainty of the inputs. The active Earth surface reservoirs of carbon (ocean, atmosphere, biomass, and soils) contain ca. $3.5 \times 10^6 \text{ Tmol of C}$ (58), so these fluxes imply mean residence time of C in the active surface reservoirs with respect to the long-term input–output fluxes of 8 to $9 \times 10^4 \text{ y}$. The accumulation of carbon-bearing marine sediments is partially offset by subduction (7, 59). Current subduction of carbonate-rich sediments is mostly in the Central-N. South America, Kermadec-Solomons, and Indian Ocean regions while substantial subducting plate length in other regions has carbonate-poor sediment (13, 60). Evidently, the rate of carbonate destruction by subduction is somewhat limited by the sedimentation history of

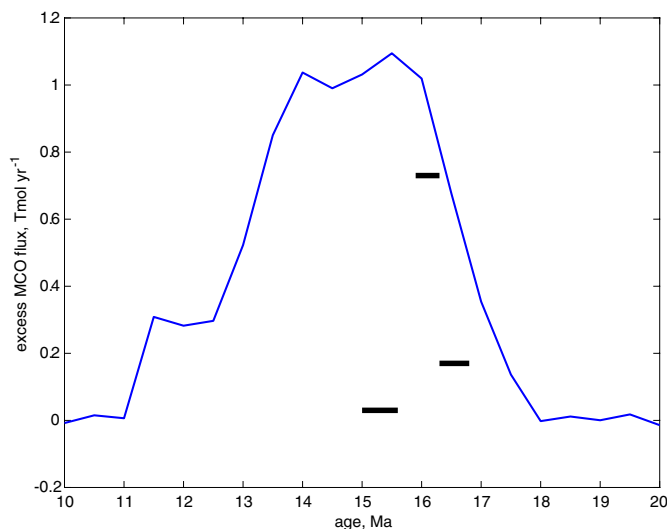


Fig. 6. Excess organic carbon burial flux (Tmol yr^{-1}) associated with MCO $\delta^{13}\text{C}$ anomaly (blue curve). Black bars are estimated emissions from the three main phases of CRB basalt eruption (51), who estimated a total CRB input of $4,880 \pm 790 \text{ Pg C}$ ($4.1 \pm 0.7 \times 10^5 \text{ Tmol}$). The integrated organic carbon burial anomaly from 11 to 18 Ma is ca. $4.3 \times 10^6 \text{ Tmol}$.

the subducted plate, with broad regions of the subducting Pacific ocean plates below the CCD. The deep CCD of the Indian Ocean (61) promotes carbonate subduction. Recent estimates of sedimentary organic and carbonate subduction rates are $\approx 1.1 \text{ Tmol yr}^{-1}$ and 4.0 to 4.8 Tmol yr^{-1} respectively (13, 60, 62); there is additional subduction of 0.5 to 1 Tmol yr^{-1} of carbonated AOC that also contains 0.1 to $0.25 \text{ Tmol } C_{\text{org}}$ (22, 63). The rate of subduction of AOC carbonate could be higher than the present rate of formation of AOC because the mean age of subducting crust is ca. 60 Ma , (64) and AOC carbonate contents were higher in the past (22). With subduction fluxes $(J_{\text{org}}^{\text{sub}} + J_{\text{carb}}^{\text{sub}}) = 6.25 \pm 2.0$, the total carbon budget is closed within considerable uncertainty (*net cycle* = 0.4 ± 9.9). The fluxes in Table 1 were not tuned or adjusted to achieve this result.

Overall, it appears that the budgets presented for the sedimentary carbonate and organic carbon cycles are consistent—within uncertainty—with global redox balance [this must include fluxes to and from the silicate Earth; (62)]. They also appear to be consistent with a CO_2 flux balance. Despite the potential quasi-balance in the overall redox and CO_2 budgets, it is a robust result that the sedimentary inventory of carbonate is currently growing:

$$\left(\frac{dM_{\text{carb}}}{dt}\right) = J_{\text{carb}}^{\text{bur}} + J_{\text{carb}}^{\text{AOC}} - J_{\text{carb}}^{\text{wea}} \approx 14.2 \pm 5.5 \text{ Tmol yr}^{-1},$$

where $J_{\text{carb}}^{\text{wea}}$ includes total carbonate weathering. Because the uncertainties on key terms in the organic carbon subcycle are larger, it is plausible that the sedimentary inventory of reduced carbon is also growing, but the net growth is not well-resolved with current data:

$$\left(\frac{dM_{\text{org}}}{dt}\right) = J_{\text{org}}^{\text{bur}} + J_{\text{org}}^{\text{AOC}} - J_{\text{org}}^{\text{ox}} - J_{\text{CH}_4}^{\text{ox}} \approx 6.0 \pm 6.9 \text{ Tmol yr}^{-1},$$

where $J_{\text{org}}^{\text{ox}}$ includes both weathering and diagenetic oxidation of *OCpetro*. While the uncertainties remain large, a balanced C_{org}

budget (no net growth) would require burial rates that are on the low end of the range for both inventory and isotope-based methods, and/or weathering and oxidation rates that are on the high end of available estimates. While these scenarios cannot be ruled out, the central estimate is consistent with net growth of the C_{org} reservoir. Assuming a normal distribution there is a 76% probability that the current net burial exceeds 1 Tmol yr^{-1} . Including subduction fluxes in this overall balance, I find net accretion of sedimentary carbonate and C_{org} of 9.2 ± 5.8 and $4.6 \pm 6.9 \text{ Tmol yr}^{-1}$, respectively. The growth of both the carbonate and organic carbon reservoirs in a system where the overall carbon budget is within uncertainty of steady state is an expected consequence of conversion of the volcanic and metamorphic degassing flux to carbonate and reduced carbon in sediments.

The net accretion of carbonate is *very likely*, while once again, the larger uncertainties associated with the organic subcycle imply that net accretion is *more likely than not* but the estimate is within uncertainty (1σ) of zero. Among other uncertainties, the subduction estimates from refs. 13, and 60 are for sediment delivered to the trench, but how much of this material is subducted to the mantle vs. accreted to overriding plate is uncertain, thus both estimates should be viewed as upper limits for actual sediment subduction to the mantle. Given that the mean age of subducting lithosphere during the Cenozoic has been $\approx 60 \text{ Ma}$, there need to be no expectation of steady state between sediment accumulation and subduction. For example, biogenic sediment from the eastern Pacific equatorial region must travel $11,000 \text{ km}$ before it could be subducted in the Kurile-Japan sector, barring plate reorganization over the next 150 My .

The net accretion of carbonate is consistent with but is not required for late Cenozoic declines in ocean-atmosphere CO_2 . While there need be no imbalance in the carbonate-silicate system to drive decreasing Neogene CO_2 (21), a slight negative imbalance is allowable (65). Similarly, the less certain but likely net accretion of sedimentary organic matter is consistent with declining $p\text{CO}_2$. In both cases, the relevant question is not whether the carbonate or organic carbon reservoirs grow, but does the net growth exceed degassing? The estimates here cannot resolve that question because any differences are well within uncertainty of the fluxes. Growth of the sedimentary C_{org} reservoir is also consistent with a different isotope mass balance model that yielded an average accretion rate of the C_{org} reservoir $\approx 1 \text{ Tmol yr}^{-1}$ since the mid-Miocene (40). Both approaches imply net generation of O_2 over the late Cenozoic. While increased sulfide oxidation has been proposed to be a Neogene O_2 sink (66), the rate of change in seawater $[\text{SO}_4^{2-}]$ and $\delta^{34}\text{S}$ place strong limits on the net change in the reduced S reservoir and imply average Neogene O_2 consumption by the sedimentary sulfur cycle $\leq 0.4 \text{ Tmol yr}^{-1}$ (21). The observation of decreasing rates of oceanic crust alteration over the Cenozoic (22) may also imply decreasing rates of Fe oxidation and an associated decrease in O_2 consumption, but this has yet to be quantified. Before $800,000 \text{ ka}$ there are no direct measurements of atmospheric O_2 (67). An overall late Cenozoic increase in atmospheric $p\text{O}_2$ prior to the mid-Pleistocene is an entirely plausible but still uncertain consequence of changes in the sedimentary C_{org} and sulfide balances and in rates of oceanic crust oxidation.

Summary and Conclusions

The stable isotope- and inventory-based estimates for organic carbon burial can be reconciled using a weighted average for the $\delta^{13}\text{C}$ of inputs to the oceans from sedimentary, volcanic, and crustal sources, yet important uncertainties remain. The widely used

inventory estimates are largely based on a >40-y-old dataset that has not been substantially updated.

The deposition of both carbonate and organic matter in marine sediments likely exceed current rates of weathering from their older sedimentary reservoirs. This is essentially a given for carbonate deposition that must integrate fluxes from both carbonate and silicate weathering [e.g., the BLAG model, (1)]; the assessment of net growth of the sedimentary carbonate reservoir is *very likely*. The new estimate of increase in the sedimentary organic carbon reservoir—*more likely than not*—is consistent with an earlier but differently constructed isotope-based model and with possible late Cenozoic increases in atmospheric pO_2 (40). Estimates of the present rates of destruction of carbon-bearing sediments at subduction zones do not fully offset the weathering-sedimentation imbalance, implying net accretion of carbonate and possibly organic carbon in the Late Cenozoic sedimentary reservoir. Burial rates for both carbonate and organic carbon in marine sediments have increased since 35 Ma while destruction rates by processes including subduction have apparently not kept pace.

The redox and CO_2 budgets presented here are within uncertainty of balance. The net growth of the sedimentary carbon reservoirs during the late Cenozoic is associated with little if any change in the much smaller ocean-atmosphere carbon reservoir (21), implying efficient feedback mechanisms for the stabilization of pCO_2 and a close net balance of CO_2 sources and sinks. Any *apparent* net imbalances in the CO_2 budget are likely the result of insufficiently well-characterized fluxes, and not indicative of an actual budget imbalance which cannot be reconciled with a stable ocean-atmosphere CO_2 reservoir since at least 25 Ma. Consequently, it is difficult to reconcile low estimates of degassing with current observations of silicate weathering rates. The net balance of the redox budget is partly dependent on the oxidation of CH_{4-geo} because its high oxidative demand. Both the CO_2 and redox balances emphasize the critical role that geogenic methane has in the carbon cycle.

What can be done to reduce the uncertainties in “closing” the carbon cycle? There are durable uncertainties in any attempt to do so. Revisiting the organic carbon burial flux with new data on C_{org} accumulation rates appears promising. The current isotope-based uncertainty is 41% *rsd* (relative SD), an improvement over (30) original rough estimate of $\pm 50\%$ but insufficient to resolve some important questions about the organic carbon subcycle. If the uncertainty on J_{org}^{bur} could be reduced to 30% *rsd* it would be possible to resolve net growth of the C_{org} reservoir, even if the uncertainties for the input terms do not change. Improved estimates of intracontinental rift and metamorphic degassing could be very helpful but are challenging because of their diffuse character. The geogenic methane flux can play an important role in the overall carbon, CO_2 , and redox budgets. Assessing the reasons for the stark differences between ^{14}C -based methods that yield low CH_{4-geo} fluxes and other

methods that yield much higher fluxes appears to be an important goal that will improve assessment of both the overall organic carbon mass balance and global redox balance. If the low range of published CH_{4-geo} oxidation rates are adopted this would imply greater growth of the C_{org} reservoir but pose challenges for the global redox budget. Similarly, why do some biogeochemical model estimates for the C_{org} burial flux (e.g., ref. 33) so greatly exceed inventory and isotope mass balance models? High rates of marine net primary production and addition of C_{org} to marine sediments are spatially associated with high rates of oxic respiration (68) so the net long-term input is once again a small difference between active biogeochemical processes.

Simple consideration of the combined mass balance of carbonate and silicate weathering implies that carbonate sedimentation will always exceed carbonate weathering and result in net growth of the sedimentary carbonate reservoir. Subduction of carbonate can buffer this growth, but at present subduction is only consuming about one third of the net carbonate reservoir growth. Unless carbonate subduction rates are high, we may expect that geologically significant periods of net carbonate accretion and growth of the sedimentary carbonate mass are not uncommon. Exceptional events, like the development of the end-Proterozoic Great Unconformity, are apparently able to destroy much of the continental sedimentary mass, leading to a step function in the mass-age distribution of preserved sediments at the end of the Proterozoic (69). Events such as these may transfer enough sediment to the deep ocean where it can subducted to reverse growth of the sedimentary carbon reservoirs. A similar mass balance applies to C_{org} , where burial currently appears to exceed weathering but uncertainties in the organic carbon subcycle remain large and the net flux cannot yet be resolved with confidence. The likely net growth of the sedimentary organic carbon reservoir was proposed as the main mechanism for the long-term oxidation of the Earth's surface (6). The results here are consistent with such a role for sedimentary carbon growth; subduction of reduced carbon may also play a role in long-term oxidation (59, 62). In the past subduction along the carbonate-rich Tethyan margin may have offset more of the sedimentary inputs, and in the future subduction along the carbonate-rich Atlantic margin could do the same, but at present both the reduced and oxidized reservoirs of sedimentary carbon are growing. The results here emphasize the non-steady-state nature of the sedimentary carbon reservoirs.

Data, Materials, and Software Availability. Previously published data were used for this work (13, 36, 37, 42).

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