

# The Carbon Cycle in the Mantle

## Implications for timescales, geochemistry, and mantle convection

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### Abstract

Though the total carbon content of the mantle is largely unknown, the isotopic signatures of its sources and sinks suggests much about how the mantle operates. Together, geochemical and mineralogical analyses of a new diamond, a compendium of studies of the magnitude of carbon fluxes into and out of the mantle, and a simple geophysical model suggest that the mantle acts as two interacting reservoirs of carbon: subducting slabs (the reservoir for depleted carbon) descend deep into the bulk mantle (the enriched-carbon reservoir) to possibly as deep as the core-mantle boundary. These reservoirs mix to a small degree; that degree is a function of the isotopic composition of the bulk mantle ( $\delta^{13}\text{C}$  from -8 to -3.5‰) and the residence time of carbon in the mantle (1-10 Gyr). The residence time is a function of the net flux out of the mantle, which is itself a sum of seafloor spreading rates, oceanic sediment deposition rates, calcium carbonate precipitation rates, and arc volcanism fluxes. This paper summarizes many studies of these fluxes to estimate those above quantities relevant to mantle convection.

### Introduction

The mantle is the largest reservoir of carbon on earth, containing more than 90% of earth's carbon by some estimates, but its relatively slow fluxes compared to those of the ocean-atmosphere and crustal systems make it less studied and less well understood. Direct measurements of the mantle are of course impossible, and while a number of potential deep carbon-containing materials have been identified, the amount of carbon in them is largely unknown. Many of these materials, such as silicates, sulfides, and oxides, can contain carbon in only trace proportions, but the sizes of the reservoirs make the overall carbon quantity potentially significant (Hazen et al., 2012). Despite the uncertainty about the mantle's composition, its size allows us to study it by many techniques, including seismology and tomography; mineralogy; ocean geochemistry; and the geology of mantle-surface access points like mid-ocean ridges, subduction zones, and volcanoes. Taken together, the multifarious studies can draw a broad picture of the mantle.

This paper focuses on the geologic and geochemical studies of the mantle-surface access points, and what we can infer about mantle fluxes and reservoirs over geologic time.

### Reservoirs

By various estimates, the mantle holds between  $6 \times 10^{17}$  kg and  $4 \times 10^{20}$  kg of carbon (Sleep and Zahnle, 2001; Javoy et al., 1982; Coltice et al., 2004). This is three to six orders of magnitude more carbon than is stored in the atmosphere-ocean system, and one to one hundred times more than that stored in the earth's crust. Figure 1 illustrates this on a logarithmic scale.

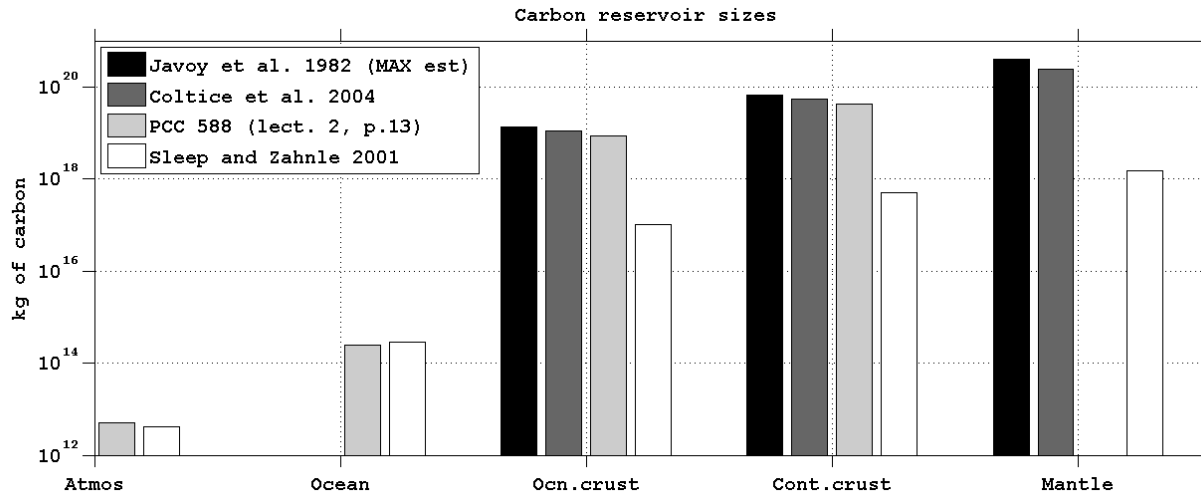


Figure 1: The amount of carbon held in the various reservoirs on earth, plotted on a logarithmic scale. Schidlowski (1987) defines marine bicarbonate as a single reservoir, the largest of the exosphere. This is not in disagreement with the plotted reservoirs, as marine bicarbonate occurs mostly in oceanic crust but is also uplifted into continental mountain ranges, like the Himalaya.

The amount of the mantle carbon that has been cycled through the exosphere<sup>1</sup> is similarly debated. We know from concentrations of radiogenic noble gases that the earth underwent a catastrophic degassing of volatile elements in its early history. Since carbon is a volatile element, without a stable mineral state in the mantle, carbon too would have entered the atmosphere in large quantities, with implications for the development of life on earth (Marty and Jambon, 1987). Either is possible: if carbon did largely outgas before continents formed, the recycling rate of carbon back to the mantle would have been 4-9 times quicker than it is today since plate tectonics were sped up by a factor of at least 4-9 in the Archean era, due to the earth's higher heat output then (Sleep and Zahnle, 2001). Simple calculations using the mantle carbon reservoir size,<sup>2</sup> the exosphere reservoir size,<sup>3</sup> and the elapsed time between outgassing and continent formation at 3.9 Ga (Schidlowski, 1987) show that the Archean recycling rate via subduction needed to be 7-50 times higher than it is today. This is within the range of the expected 4-9 times higher, though with little overlap. Marty and Jambon (1987) conclude, therefore, that a catastrophic mantle outgassing event was unlikely, and that a stable mineral phase must exist for carbon to have stayed in the mantle when the other volatiles outgassed.

## Fluxes

Carbon from the mantle first enters the exosphere at ocean ridges, where seafloor spreading brings magma up from the mantle and lays it down as mid-ocean ridge basalt (MORB), grow-

<sup>1</sup>The exosphere is defined as the volume outside the mantle: the crust, ocean, atmosphere, and biosphere.

<sup>2</sup>This study used  $(2.3-4.7) \times 10^{19}$  kg.

<sup>3</sup>This study used  $(5.5-9.5) \times 10^{17}$  kg.

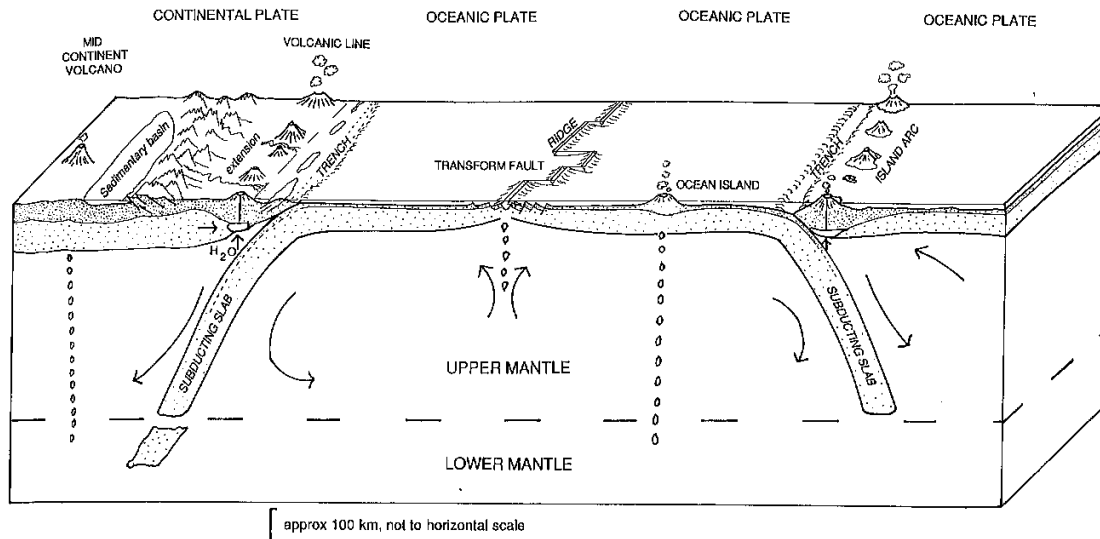


Figure 2: Diagram showing the seafloor spreading process (center), hotspot volcanism (right of center), and subduction and arc volcanism at subduction zones (left and right). Not illustrated are the oceanic deposition of organic sediments onto the crust and of carbonates into veins within it. From Fowler (1990, p. 255).

ing the oceanic plate. From there they begin their slow ( $10^{-1}$  to  $10^{-2}$  m/yr) undersea journey, during which they collect seafloor sediments on their way to collide with continental tectonic plates. Here, the oceanic plate subducts under the continent. Figure 2 illustrates this process.

The fate of the oceanic plate is matter of ongoing debate: tomographical evidence (e.g. Grand et al. (1997); Ren et al. (2007)) suggests that the plate continues to descend most of the way through the mantle to reach the core, while thermal and mineralogical arguments (e.g. Kellogg et al. (1999); Hamilton (2003); Anderson (2001)) imply that plates are halted at the transition zone, the boundary between the upper and lower mantle layers at about 660 km depth. These are the opposing arguments of mantle convection models: if plates can descend to the core, then whole-mantle convection is possible; if not, then convection must occur in separate cells above and below the transition zone.

Regardless of the type of mantle convection, the bulk of the slab continues its descent to at least 660 km. But a fraction of its carbon and other volatile materials rise to the surface again through back-arc volcanoes. Other volcanoes (from hotspots) also provide a conduit for mantle material to reach the surface, although geochemical studies (e.g. Sun and McDonouch (1989)) show that the hotspot material must originate from the deep mantle, and that the overall contribution of hotspots to the mantle carbon budget ( $2.5 \times 10^6$  kg yr $^{-1}$ ) is small (Sano and Williams, 1996).

The fluxes between the exosphere and the mantle have proven to be difficult to measure precisely or consistently. Here I present a literature review of the existing measurements for each flux. I follow the “balanced cycle” of Sleep and Zahnle (2001), which combines the continental crust, atmospheric, and oceanic reservoirs. I additionally simplify the weathering cycle

so that the only input into the continental-atmospheric-oceanic reservoir is volcanism, and the only output is ocean sedimentation.

## Mid-ocean ridge basalt fluxes

Carbon exits the mantle to the exosphere at mid-ocean ridges in two ways: by being laid down as basalts on the oceanic crust, and by outgassing to CO<sub>2</sub> which dissolves in the ocean water. Measurements of carbon content made by heating basalts from the East African Rift Valley and MORBs indicate that as much as 30-65% of carbon is outgassed (Gerlach, 1989). This carbon is later deposited on the oceanic crust in carbonate veins, in a process termed seafloor alteration (Shilobreeva et al., 2011).

The standard method for estimating carbon content of freshly-upwelled basalts is through the <sup>3</sup>He isotope tracer, which is used because the <sup>3</sup>He flux is well-known and the C/<sup>3</sup>He ratio is thought to be unfractionated during mantle degassing. With a lack of fractionation, the MORB carbon flux is found to be  $2.6 \times 10^{10}$  kg yr<sup>-1</sup> (Marty and Jambon, 1987). This measurement and flux has been called the “most reliable” (Sano and Williams, 1996) in part because it agrees with independent carbon flux measurements based on hydrothermal vents (Gerlach, 1989).

To account for the differing δ<sup>13</sup>C signatures of the mantle (-5‰) and some MORBs (as low as -26‰), though, Javoy et al. (1982) argue that the C/<sup>3</sup>He ratio is fractionated: they calculate a fractionation factor of 0.014, suggesting that much more carbon stays in the mantle than is outgassed to MORBs or the ocean water. The resulting carbon exiting the mantle through MORBs is just  $6-70 \times 10^9$  kg yr<sup>-1</sup> (Marty and Jambon, 1987).<sup>4</sup>

A mineralogical model of the partial melting of carbon at mid-ocean ridges suggested that the MORBs have a much higher carbon content than previously thought (120-1200 ppm), giving a MORB carbon flux of  $(0.12-3.4) \times 10^9$  kg yr<sup>-1</sup>, an order of magnitude higher than other measurements of basalts. This large flux would suggest that the mantle reservoir of carbon could overturn in 1-4 Gyr – that is, at least once in the 4.5 Gyr age of the earth (Dasgupta and Hirschmann, 2006).<sup>5</sup>

## Seafloor alteration fluxes

Carbon that is outgassed from mid-ocean ridges as CO<sub>2</sub> enters the seawater as an inorganic component. In the tens to hundreds of millions of years between the oceanic plate’s birth at the spreading center and its death by subduction, the plate collects that seawater carbon in veins

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<sup>4</sup>This number differs between the paper that calculated it, Javoy et al. (1982), and a paper that cites it and places it into context with its own MORB measurements, Marty and Jambon (1987). The difference is of two orders of magnitude: Javoy et al. (1982) find  $6-70 \times 10^{11}$  kg yr<sup>-1</sup>, which is actually *greater* than the unfractionated C/<sup>3</sup>He MORB carbon flux. Unfortunately, this seems to be a common occurrence in the mantle carbon cycle literature: the fluxes cited by Coltice et al. (2004) also did not agree with the studies they cited, Alt and Teagle (1999) and Staudigel et al. (1989) (seafloor alteration), and Sano and Williams (1996) (arc volcanism). Coltice et al. (2004) do cite the MORB carbon flux from Marty and Jambon (1987) correctly.

<sup>5</sup>Note that this is not in direct disagreement with the conclusions of Marty and Jambon (1987) (see Reservoirs section), who argue that much of the mantle’s carbon stayed in the mantle during the early-earth catastrophic outgassing event. Though the high-recycling-rate conclusion of Dasgupta and Hirschmann (2006) requires the mantle carbon to *not* be primordial, it allows the carbon to cycle to the exosphere gradually rather than catastrophically.

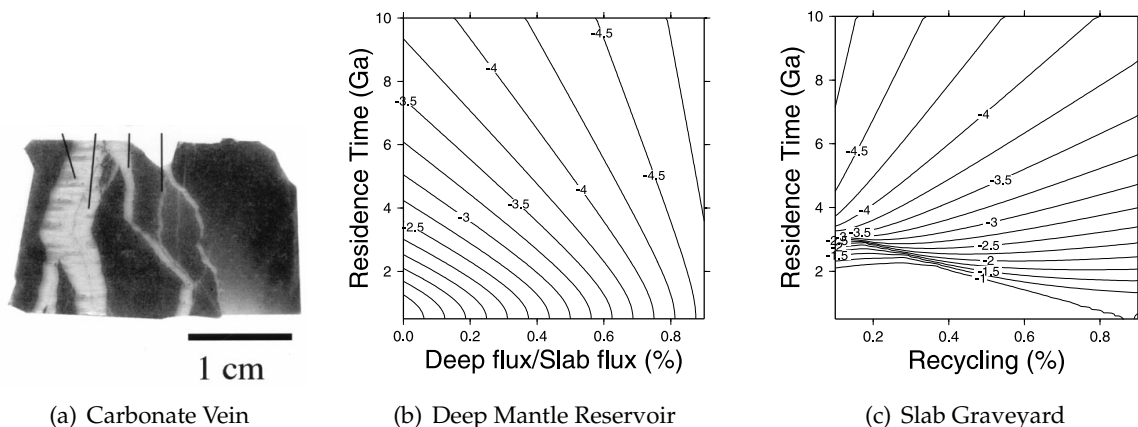


Figure 3: (a) Photograph of a 165 million-year-old rock from western Pacific oceanic crust, showing the deposition of  $\text{CaCO}_3$  in veins. From Alt and Teagle (1999). (b) and (c) Models of Coltice et al. (2004). Residence time is a proxy for mantle reservoir size:  $M = \tau \Phi$ , where  $\tau$  is residence time and  $\Phi$  is MORB flux, approximately  $10^{10} \text{ kg yr}^{-1}$ . Contours show the  $\delta^{13}\text{C}$  of the bulk mantle at each parameter point. (b) Model of mixing ratio between the deep reservoir and the reservoirs that subducting slabs penetrate. “Flux” refers to the carbon flux supplied to MORBs. (c) Model of slab segregation within the mantle. Recycling percentage is the fraction of subducted slabs that do not descend all the way to the “slab graveyard” at the core-mantle boundary: this mass reenters the mantle carbon cycle.

which fill with calcium carbonate precipitates. This can be commonly observed in mountains made of uplifted seafloor sediments (e.g. the Olympics) and is illustrated in Figure 3(a). This is termed “low-temperature seafloor alteration” since it happens at geologically cool ( $< 60^\circ\text{C}$ ) temperatures. A survey of carbonates of various ages on the Pacific plate showed that the plate becomes essentially saturated with carbonates after 10-100 million years (Alt and Teagle, 1999).

Seafloor alteration provides a mechanism for inorganic carbon to enter the mantle by subduction. It is of similar size to, if not larger than, the deposition by biological sediments on the ocean floor. Seafloor alteration fluxes are calculated as the product of the weight percent of  $\text{CO}_2$  in carbonate veins of oceanic crust (measured from cores of the oceanic crust), crustal density, and the rate of seafloor production and subduction (of order  $0.5 \text{ km}^3 \text{ yr}^{-1}$ ). Calculations from cores in all oceans and of various ages agree reasonably well: the net flux of carbon onto oceanic crust (and eventually the mantle) is reported as  $2.8 \times 10^8 \text{ kg yr}^{-1}$  (Alt and Teagle, 1999; Sleep and Zahnle, 2001),  $(2.1\text{-}2.7) \times 10^8 \text{ kg yr}^{-1}$  (Shilobreeva et al., 2011), and  $(1.8\text{-}2.4) \times 10^8 \text{ kg yr}^{-1}$  (Staudigel et al., 1989) – numbers which agree to within a factor of three.<sup>6</sup>

More chemically-based models calculate the carbonate deposition rate as a function of hydrothermal flux, which is calculated from the concentration of magnesium in sediments. These estimates tend to produce lower deposition rates – warmer waters have low deposition rates (total carbon flux into carbonate veins  $(1.4\text{-}8.6) \times 10^6 \text{ kg yr}^{-1}$ ), while the deposition rates in

<sup>6</sup>Coltice et al. (2004) report seafloor alteration fluxes two orders of magnitude higher than these, citing the work of Staudigel et al. (1989) and Alt and Teagle (1999) but quoting the values incorrectly (see Footnote 4).

cooler waters ( $1.4 \times 10^8 \text{ kg yr}^{-1}$ ) agree reasonably well with the weight-percent estimates (Sleep and Zahnle, 2001).

## Subduction fluxes

The total return flow of carbon to the mantle is the sum of the precipitation of carbonate into veins and the deposition of organically derived sediments onto the oceanic crust. Calculation of carbon-containing sediment on the subducting slab is simple and similar to the calculation of the carbon production rate at MORBs: the flux is the product of the sediment thickness, sediment density, fraction of carbon present, and the subduction rate. Estimates by this method span an order of magnitude, from  $1.2 \times 10^{10} \text{ kg yr}^{-1}$  (Coltice et al., 2004) to  $(2.8\text{-}5.6) \times 10^{11} \text{ kg yr}^{-1}$  (Javoy et al., 1982).

Alternatively, one may calculate the total subduction flux as the sum of the vein carbonates from seafloor alteration and the net deposition of organic kerogens. The organic flux amounts to about  $1 \times 10^{11} \text{ kg yr}^{-1}$ , about  $10^{-2} - 10^{-3}$  of global primary production (Schidlowski, 1987). This agrees well with the above subduction-rate estimates. It also suggests that biological productivity is one to three orders of magnitude more important than seafloor alteration, which seems to be a matter of contention among the scientists of each field.<sup>7</sup>

The subducted carbon may not continue into the mantle: a fraction of the mass of a subducting slab returns to the exosphere through the nearby arc volcanoes driven by subduction. Since carbon is a volatile element, it is prone to melt and subsequent exhalation by volcanism.

## Arc volcanism fluxes

Sano and Williams (1996) measured  $^3\text{He}$  fluxes from arc volcanoes and converted them to carbon fluxes using the  $\text{C}/^3\text{He}$  ratio. Unlike Javoy et al. (1982), they assumed this ratio is unfrac-tionated during magma outgassing. They found a total flux of  $2.6 \times 10^8 \text{ kg yr}^{-1}$ , about 90% of which was sourced from the mantle. The remaining  $2.5 \times 10^7 \text{ kg yr}^{-1}$  was recycled from the subducting oceanic plates, thus diverting that carbon from returning to the mantle.

This proportion is higher than other studies have estimated: Sleep and Zahnle (2001) found that 10% of subducted carbon rose back to the exosphere through arc volcanoes; Shilobreeva et al. (2011) calculated 40%, and Coltice et al. (2004) almost 50%. Regardless, arc volcanism carbon fluxes are always smaller than subducted carbon fluxes, and thus at least some of the exogenic carbon returns to the mantle.

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<sup>7</sup>Shilobreeva et al. (2011), a study of carbonate veins, found that the organic / inorganic sediment ratio was approximately 3 to 1. Staudigel et al. (1989), on the same "carbonate team", found a ratio more like 1 to 1, as did the review of Sleep and Zahnle (2001). On the other hand Coltice et al. (2004), a geophysical paper, found a ratio of 1 to 4. Kump, Kasting, and Crane (2004), the textbook quoted by a PCC 588 lecture slide, also finds a 1 to 4 ratio. No paper that compiled both inorganic and organic seafloor fluxes found a difference even approaching the order of magnitude suggested here.

Table 1: *Compiled fluxes into and out of the mantle. Each row represents a different set of fluxes, summarized from three different studies (“high-magnitude”, Coltice et al. (2004) and “earth-age-averaged”, Shilobreeva et al. (2011)) or reviews (“geologic”, Sleep and Zahnle (2001)). Fluxes are in  $\text{kg yr}^{-1}$  and are defined with respect to the mantle: positive is into the mantle. Arc stands for arc volcanism. The subduction category is the sum of carbonate-containing crustal veins (“veins”) and organic seafloor precipitates (“sediment”). The total flux for each set shows either a net exhalation from (-) or deposition to (+) the mantle.*

	Fluxes out of mantle			Subduction into mantle			Total Flux
	MORB	Hotspots	Arc	Veins	Sediment	Total	
High-mag	$-2.4 \times 10^{10}$	$-2.5 \times 10^6$	$-2.0 \times 10^{10}$	$3.0 \times 10^{10}$	$1.2 \times 10^{10}$	$4.2 \times 10^{10}$	$-2.0 \times 10^9$
Geologic	$-2.1 \times 10^8$	$-2.5 \times 10^6$	$-6.6 \times 10^7$	$1.3 \times 10^8$	$2.1 \times 10^8$	$4.9 \times 10^8$	$+2.1 \times 10^8$
Earth-age-avg	$1.7 \times 10^8$	$2.5 \times 10^6$	$1.3 \times 10^8$	$2.4 \times 10^8$	$7.4 \times 10^7$	$3.1 \times 10^8$	$+7.5 \times 10^6$
	$1.7 \times 10^9$						$-1.5 \times 10^9$

## Balance of fluxes

The myriad methods for determining the four basic carbon-exospheric fluxes yield widely differing results. This is discouraging, as it is not the fluxes themselves but their total balance that we are interested in. In Table 1 I attempt to balance the carbon budgets for three different sets of fluxes: a “high magnitude” set quoted by Coltice et al. (2004),<sup>8</sup> a “geologic” set collected in the review by Sleep and Zahnle (2001), and an “earth-age-averaged” set summarized by Shilobreeva et al. (2011). Though different techniques were used to assemble the fluxes, each set contains fluxes of the same magnitude and is in near-balance.

Unfortunately, despite being in near-balance, each set predicts a different net flux into or out of the mantle. In two cases the net flux is of order  $10^9 \text{ kg yr}^{-1}$  out of the mantle, and in the other two cases (depending on the MORB flux) the net carbon flux is into the mantle, but of lower magnitude ( $10^7$  to  $10^8 \text{ kg yr}^{-1}$ ).

## Net mantle-to-exosphere flux

The terrestrial biosphere requires that the net carbon flux averaged over the age of the earth be negative, that is out of the mantle. The total biosphere mass is of order  $10^{18} \text{ kg}$  (Sano and Williams, 1996) or  $10^{19} \text{ kg}$  (Coltice et al., 2004; Javoy et al., 1982); if it accumulated over approximately 4 Gyr, then the net flux out of the mantle needs to be of order  $10^8$  to  $10^9 \text{ kg yr}^{-1}$ , in agreement with the high-magnitude flux set based on Coltice et al. (2004) and the earth-age-averaged flux set (with a high MORB carbon flux) based on Sleep and Zahnle (2001).

<sup>8</sup>Recall from the Mid-Ocean Ridge Basalt Fluxes section that this paper incorrectly cited three studies’ fluxes.

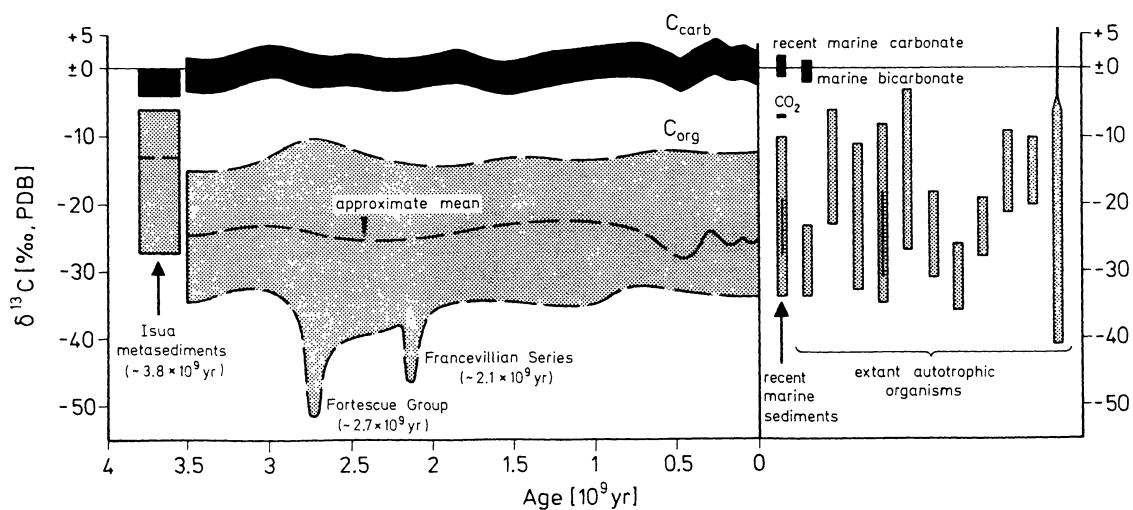


Figure 4: Apart from excursions of much shorter duration (10 Myr) than mantle timescales, the  $\delta^{13}\text{C}$  signatures of both inorganic sediments (carbonates) and organic sediments (kerogens) have been quite constant over time. From Schidlowski (1987).

### Evolution over geologic time

As discussed in the Reservoirs section, plate tectonics operated more quickly on the hot early earth (Sleep and Zahnle, 2001). Thus, the carbon cycle would have been sped up then and without a change from today's imbalance, there would be much more carbon in the exosphere than there is today. The evolution of the biosphere and its waxing and waning over time must therefore exert an important control on the long-term carbon cycle. Indeed, the relative sizes of the organic and inorganic sedimentary exogenic reservoirs of carbon can be seen to vary through geologic time by looking at their  $\delta^{13}\text{C}$  timeseries (Schidlowski, 1987).

### Geochemistry

Analysis of MORBs shows that the upper mantle has a  $\delta^{13}\text{C}$  value between  $-8$  and  $-3.5\text{‰}$ , a value which has been essentially constant throughout earth's history (Coltice et al., 2004; Javoy et al., 1986). The mantle carbon is biologically fractionated in the exosphere: the kinetic isotope effect during photosynthesis makes organisms depleted in  $^{13}\text{C}$  (enriched in the lighter  $^{12}\text{C}$ ). This fractionation is furthered in C4 photosynthesis, where thermodynamically controlled equilibrium fractionations preferentially select  $^{12}\text{C}$  in bicarbonate pathways. Thus, organic compounds are quite depleted in the heavier isotope and have  $\delta^{13}\text{C}$  signatures of  $-24$  to  $-28\text{‰}$  (Schidlowski, 1987). This range is commonly approximated as  $-25\text{‰}$ . In contrast, carbonate sediments carry an abiogenic  $\delta^{13}\text{C}$  near  $0\text{‰}$  (Coltice et al., 2004).

As with MORBs, the  $\delta^{13}\text{C}$  record for organic and inorganic materials is also remarkably constant over time, as shown in Figure 4. These sediments together comprise the subduction flux;



the organic to inorganic ratio of approximately 1 to 4 (see Seafloor Alteration Fluxes footnote) suggests that the overall  $\delta^{13}\text{C}$  of subducted carbon is 1‰. This sets up a paradox: the mantle and sedimentary reservoirs have different  $\delta^{13}\text{C}$  values, yet both mantle and sedimentary  $\delta^{13}\text{C}$  are constant over time. The implication is that either one reservoir is sufficiently large that it can buffer the other reservoir's carbon signature without an observable change of its own  $\delta^{13}\text{C}$ , or that the two reservoirs stay separate in the mantle.

## Mantle Convection

Coltice et al. (2004) develop simple time-dependent descriptions of the isotopic signature of the mantle and subducted reservoirs for each case. For the "buffer reservoir" model, they find that the upper mantle is likely insufficient to act as the buffer: it would need to contain at least  $2.4 \times 10^{20}$  kg C, which is on the upper end of their estimates for the entire mantle. They propose instead a deep-mantle reservoir that holds primordial carbon ( $\delta^{13}\text{C}$  of -5‰) and accounts for about half of the mass of the mantle. This model is consistent with a model for layered mantle convection that explains seismic anomalies at depth (Kellogg et al., 1999). The MORB carbon is sourced partly from this reservoir and partly from recycled sediments; the  $\delta^{13}\text{C}$  is determined by this mixing fraction and the total carbon mass in the deep mantle, as shown in Figure 3(b).

In contrast, the separate reservoir model allows the cold, dense subducting slabs to descend all the way to the bottom of the mantle, where they would lie stably for geologic time in a "slab graveyard" of sorts. Indeed, their negative thermal buoyancy and numerous tomographical observations (Grand et al., 1997; Ren et al., 2007) suggest that this happens. Figure 3(c) shows how the fraction of the slab carbon that is recycled into MORBs affects the bulk  $\delta^{13}\text{C}$  of the mantle: for a residence time of 2 Gyr (i.e. a total mantle carbon content of  $5 \times 10^{19}$  kg, well within estimates), 60% of the slab carbon must be segregated at the core-mantle boundary (40% of the slab carbon is recycled). This is an attractive model because the accumulation of this amount of oceanic crust<sup>9</sup> at the core-mantle boundary could explain the mass of the D" seismic reflector there (Coltice et al., 2004).

The "slab graveyard" model of Coltice et al. (2004) may also explain the  $\delta^{13}\text{C}$  of some singular diamonds. All diamonds are sourced from deep in the mantle; they are exhumed rapidly<sup>10</sup> to the surface in kimberlite formations. Most diamonds have  $\delta^{13}\text{C}$  near -5‰, identical to that of MORBs and the bulk mantle, but a minority of diamonds are depleted in  $^{13}\text{C}$ , having  $\delta^{13}\text{C}$  from -10 to -30‰. Previously, these light diamonds were thought to be upper-mantle-derived, thus taking their light  $\delta^{13}\text{C}$  from subducted sediments (Javoy et al., 1986). All known diamonds sourced from the deep mantle had MORB-like  $\delta^{13}\text{C}$  until recently.

Walter et al. (2011) made a major discovery of deep-mantle-sourced diamonds that are isotopically light. The suite of mineral inclusions they identified in these 100 million-year-old Brazilian diamonds show definitively that they originated in the lower mantle (between 1400 and 700 km depth), while their  $\delta^{13}\text{C}$  range of -5 to -24‰ show a clear contribution from biologic

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<sup>9</sup>This assumes that the bulk oceanic crust is recycled at the same percentage as the carbon within it, i.e. that carbon has a similar volatility to the bulk oceanic crust. This seems like a poor assumption since carbon is much more volatile than average earth minerals.

<sup>10</sup>Geologically rapidly: their exhumation takes tens of millions of years.

sediments transported to the deep mantle by subducted slabs. This has important implications for mantle convection: if subducting slabs can penetrate the transition zone phase boundary at 660 km depth and enter the deeper mantle, the mantle must be well-stirred and convect as one unified cell.<sup>11</sup>

## Conclusion

Though our knowledge about the total amount of carbon that exists in various mineral states in the mantle is limited, we have been able to measure the various fluxes of carbon into and out of the mantle, with some success. A wide array of studies of these fluxes were made in the 1980s, with different measurements of the same flux often yield widely varying results. Thus the total flux into the mantle is not well-known: different budgets yield different values and even different signs. We do know from the amount of accumulated carbon on the earth's surface that the net flux of carbon over the age of the earth has been of order  $10^8$  to  $10^9$  kg yr<sup>-1</sup>.

The isotopic fractionation of carbon by biological processes also has wide-reaching implications. Geological evidence shows that the fractionation has been quite constant over the age of the earth, yet the mismatch between the  $\delta^{13}\text{C}$  of the bulk mantle and of subducting sediment suggest that subducting slabs descend to a largely separate reservoir. The  $\delta^{13}\text{C}$  of diamonds suggest that this reservoir is deeper than the transition zone, and may even be at the core-mantle boundary. Thus, analysis centered on the relatively inaccessible carbon content of the mantle provide clear and simple evidence for full- rather than layered-mantle convection, one of the largest questions in geophysics.

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<sup>11</sup>The competing mantle convection hypothesis, that of two stacked layers, is unlikely and unnecessary if massive subducting slabs travel through and mix both layers.

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