The Carbon Cycle and Associated Redox Processes Through Time

John M. Hayes[1] and Jacob R. Waldbauer[2]

[1](jhayes@whoi.edu) Department of Geology and Geophysics
Woods Hole Oceanographic Institution, Woods Hole, MA 02543

[2]Joint Program in Chemical Oceanography, Woods Hole Oceanographic Institution
and Massachusetts Institute of Technology, Cambridge, MA 02139

Summary

Earth's biogeochemical cycle of carbon delivers both limestones and organic materials to the crust. In numerous, biologically catalyzed redox reactions, hydrogen, sulfur, iron, and oxygen serve prominently as electron donors and acceptors. The progress of these reactions can be reconstructed from records of variations in the abundance of ^{13}C in sedimentary carbonate minerals and organic materials. Because the crust is always receiving new CO_2 from the mantle and a portion of it is being reduced by photoautotrophs, the carbon cycle has continuously released oxidizing power. Most of it is represented by Fe^{3+} that has accumulated in the crust or been returned to the mantle *via* subduction. Less than 3% of the estimated, integrated production of oxidizing power since 3.8 Ga is represented by O_2 in the atmosphere and dissolved in seawater. The balance is represented by sulfate. The accumulation of oxidizing power can be estimated from budgets summarizing inputs of mantle carbon and rates of organic-carbon burial, but levels of O_2 are only weakly and indirectly coupled to those phenomena and thus to carbon-isotopic records. Elevated abundances of ^{13}C in carbonate minerals ~2.3 Gyr old, in particular, are here interpreted as indicating the importance of methanogenic bacteria in sediments rather than increased burial of organic carbon.

Key index words

Carbon cycle, Carbon isotopes, Atmospheric oxygen, Methanogenesis, Subduction, Mantle

Revised version, 24 January 2006, of paper presented at Discussion Meeting of the Royal Society, "Major steps in cell evolution: palaeontological, molecular and cellular evidence of their timing and global effects," London, 26 and 27 September 2005. Submitted to *Philosophical Transactions of the Royal Society B*. **This version differs from a prior revision dated 21 December 2005.** Equations 11 and 12 have been corrected. Corresponding changes have been made to some points in the discussion and to Figure 9. The conclusions are unchanged.

Together, biological and geological processes – oxygenic photosynthesis and the burial of organic carbon – get credit for producing and maintaining the O_2 in earth's breathable atmosphere. This view of the carbon cycle as the engine of environmental evolution is based on sedimentary records. The disappearance of mass-independent fractionation of the isotopes of sulfur is the most reliable indicator for the accumulation and persistence of traces of O_2 in the atmosphere beginning at about 2.4 Ga ($p_{O2} \geq 10^{-5}$ atm; Pavlov & Kasting, 2002; Farquhar & Wing, 2003; Bekker *et al.*, 2004). Biomarkers derived from lipids associated with cyanobacteria first appear in sedimentary rocks with an age of 2.7 Gyr (Summons *et al.*, 1999; Brocks *et al.*, 2003; Eigenbrode, 2004). These provide strong evidence for oxygenic photoautotrophy at that time (*i. e.*, for production of O_2 as opposed to its accumulation, persistence, and global distribution). Abundances of oxidized and reduced minerals in ancient soil profiles and sediments generally indicate a transition from weakly reducing to weakly oxidizing conditions at earth's surface soon after 2.47 Ga (Bekker *et al.*, 2004; Canfield, 2005; Catling & Claire, 2005).

But what about examining the engine itself? Records of the burial of organic carbon, which should be provided by abundances of ^{13}C in sedimentary carbonates and organic material (Broecker, 1970), could indicate the pace *and* the mechanism of oxidation. For events and processes during the past 500 Ma, carbon-isotopic records have been interpreted with considerable success (*e. g.*, Garrels & Lerman, 1981; Holland, 1984; Berner, 1991, 2004; Kump & Arthur, 1999). The same approach has been extended to Precambrian records (*e. g.*, Schidlowski *et al.*, 1975; Hayes, 1983, 1994; Knoll *et al.* 1986; Derry *et al.*, 1992; Karhu & Holland, 1996; Halverson *et al.*, 2005), but conclusions have usually been qualitative rather than quantitative. The carbon-isotopic record can be described as "consistent with" some postulated event or process, but understanding of the carbon cycle has not been complete enough to allow resolution of uncertainties or elaboration of details.

Two recent findings may change this. First, new evidence (Saal *et al.*, 2002) has led to wide agreement (*cf.* Resing *et al.*, 2004) on the rate at which C is delivered to the crust from the mantle at mid-ocean ridges. This significant reduction in uncertainties about the input allows a new approach to carbon budgets. Second, a previously overlooked output of carbon from the ocean has been recognized and quantified. Whereas earlier concepts limited the outputs to sedimentary carbonates and organic matter, the new view includes a very large flow of carbon that's taken up during the weathering of seafloor basalts. This changes the structure of the mass balances. The potential role of this production of "carbonated basalts" in the carbon cycle was first identified by Staudigel *et al.* (1989). Subsequently, Alt & Teagle (1999, 2003) have examined amounts and isotopic compositions of these carbonate minerals and discussed their importance in the modern carbon cycle. Walker (1990), Sleep & Zahnle (2001), and Nakamura & Kato (2004) have called attention to carbonation of submarine basalts as an important phenomenon during the Archaean. Bjerrum & Canfield (2004) have introduced a systematic treatment of this problem.

Our purpose here, based on those developments, is to demonstrate a new approach to studies of the carbon cycle and its effects on the global environment. Among those effects, we focus on oxidation of earth's surface over the past four billion years.

The Structure of the Carbon Cycle

A geochemical view of the carbon cycle is shown in Figure 1. The scheme chosen highlights processes that control the isotopic composition of inorganic carbon dissolved in the ocean. That carbon pool is in rough equilibrium with the atmosphere and with carbonate minerals derived from seawater. It is the senior author of our best records of how the carbon cycle has operated over the course of earth history. To interpret those records, we must consider the fluxes indicated in Fig. 1. They represent processes that are linked by balances of mass and electrons. The related equations are, at present, analytical tools rather than components of an elaborate model.

The reaction chamber in which isotopic variations are shaped is comprised of the atmosphere, hydrosphere, and C-exchanging sediments and soils. Carbon flows into that chamber from the mantle and by recycling of carbon within the crust. It leaves through burial in sediments and during weathering of seafloor basalts. If the amount of C in the reactor is constant, the inputs will be balanced by the outputs:

$$J_{\mathrm{am}} + J_{\mathrm{ar}} + J_{\mathrm{or}} + J_{\mathrm{av}} + J_{\mathrm{ov}} = J_{\mathrm{ab}} + J_{\mathrm{ob}} + J_{\mathrm{aw}} \tag{1}$$

The terms in this equation represent fluxes of carbon in moles/time. The subscripts a and o refer to inorganic and organic carbon. In detail, J_{am} is the total input of C from the mantle *via* outgassing of magmas at seafloor hydrothermal vents and at hot-spot and island-arc volcanoes; J_{ar} and J_{or} are, respectively, returns of carbonate and organic C by exposure and weathering of deposits on continents and shelves; and J_{av} and J_{ov} are returns, principally by arc volcanism, of carbonate and organic C remobilized during subduction. Among the outputs, J_{ab} and J_{ob} are the net burials of carbonate- and organic-C in marine sediments, deriving mainly from processes in surface waters but often bearing strong secondary imprints; and J_{aw} is carbonate being taken up at the seafloor during the weathering of basalts. These, and all additional definitions pertinent to this discussion, are summarized in Table 1.

A second mass balance equates incoming and outgoing ^{13}C. Its elaboration leads to a key indicator of variations in the operation of the carbon cycle. For simplicity and generality, it is often written in this form:

$$J_{\mathrm{i}}\delta_{\mathrm{i}} = J_{\mathrm{ab}}\delta_{\mathrm{ab}} + J_{\mathrm{ob}}\delta_{\mathrm{ob}} + J_{\mathrm{aw}}\delta_{\mathrm{aw}} \tag{2}$$

where J_{i} represents the summed inputs to the exogenic reaction chamber, δ_{i} represents their weighted-average isotopic composition, and the remaining δ terms represent the isotopic compositions of the indicated fluxes. In detail, a fully correct form would be:

$$J_{\mathrm{am}}\delta_{\mathrm{am}} + J_{\mathrm{ar}}\delta_{\mathrm{ar}} + J_{\mathrm{or}}\delta_{\mathrm{or}} + J_{\mathrm{av}}\delta_{\mathrm{av}} + J_{\mathrm{ov}}\delta_{\mathrm{ov}} = J_{\mathrm{ab}}\delta_{\mathrm{ab}} + J_{\mathrm{ob}}\delta_{\mathrm{ob}} + J_{\mathrm{aw}}\delta_{\mathrm{aw}} \tag{3}$$

Because values for many of the terms on the left side of this equation are inaccessible, analyses usually proceed from eq. 2, incorporating the assumptions that $J_{\mathrm{i}} = J_{\mathrm{ab}} + J_{\mathrm{ob}} + J_{\mathrm{aw}}$ and that $\delta_{\mathrm{i}} = \delta_{\mathrm{am}}$. When historical variations are considered, the latter has two components: (*i*) that mixing of recycling inputs eventually yields an unbiased sample and (*ii*) that δ_{am} is constant. Over rock-cycle time scales of 300 Myr or more, the first requirement is probably met. Second, the constancy and uniformity of δ_{am} are well supported. Independent of age of emplacement or location, diamonds from peridotitic xenoliths have $\delta = -5‰$ (Pearson *et al.*, 2004). The same value is found in carbonatites and mantle-derived basalts (Kyser, 1986; Mattey, 1987).

The task now is to provide a useful approach to interpreting observed variations in δ_{ab}, the carbon-isotopic composition of sedimentary carbonates. As has become conventional, we define the fraction of input C buried in organic form as $f \equiv J_{\mathrm{ob}}/J_{\mathrm{i}}$. Following Bjerrum & Canfield (2004), we define the fraction of total carbonate accounted for by ocean-crustal carbonates as $\lambda \equiv J_{\mathrm{aw}}/(J_{\mathrm{aw}} + J_{\mathrm{ab}})$.

Our approach to the isotopic variables differs from previous expositions. As the reference point, we choose the isotopic composition of total dissolved inorganic carbon (DIC) in marine surface waters, δ_a. The isotopic compositions of the outputs are related to δ_a by the following expressions.

$$\delta_{ab} = \delta_a - \Delta_g \tag{4}$$

$$\delta_{ob} = \delta_a - \varepsilon \tag{5}$$

$$\delta_{aw} = \delta_a - \Delta_m \tag{6}$$

where Δ_g is the globally averaged isotopic difference between surface DIC and diagenetically stabilized sedimentary carbonates. At present, for example, comparison of pre-industrial δ_a (Quay *et al.*, 2003) and average sedimentary carbonate (Shackleton, 1987) indicates $\Delta_g \approx 2$‰. Local variations in Δ_g can affect specific sedimentary records. The difference in isotopic composition between sedimentary organic carbon and DIC, ε, is principally (though not exclusively) due to isotopic discrimination during biotic carbon fixation. The sign chosen in eq. 5, with $\varepsilon > 0$ corresponding to depletion of ^{13}C in biomass, is conventional in marine biogeochemistry. Values of Δ_m will be positive when ocean-crustal carbonates are depleted in ^{13}C relative to surface waters. Reports of δ_{aw}, required to evaluate Δ_m, are rare. Alt & Teagle (2003) find $\delta_{aw} = 1.7 \pm 0.4$‰ for ocean-crustal carbonates that have formed during the past 160 Ma. The average value of δ_{ab} during the same interval (Veizer *et al.*, 1999) is 1.7‰. At present, therefore, $\Delta_m \approx \Delta_g \approx 2$‰. Other reports occasionally indicate lower values of δ_{aw} and thus suggest larger values of Δ_m but, based on associated sedimentary features, the authors uniformly attribute the depletion of ^{13}C to infrequent additions of C derived from oxidation of organic material.

Substitution of eqs 4-6 in eq. 3 and simplification of the result yields

$$\delta_{ab} - \delta_i = f(\varepsilon - \Delta_g) + \lambda(1 - f)(\Delta_m - \Delta_g) \tag{7}$$

For $\Delta_g = 0$, eq. 7 is equivalent to eq. 4 of Bjerrum & Canfield (2004). If, in addition, either or both Δ_m and λ are zero, eq. 7 becomes $\delta_{ab} - \delta_i = f\varepsilon$, the expression found in numerous prior discussions of isotopic fractionation in the carbon cycle. Does this expression indicate that Δ_m and Δ_g can be as effective as f and ε in controlling $\delta_{ab} - \delta_i$? Probably not. Their leverage is relatively small. In most circumstances, the first term, $f(\varepsilon - \Delta_g)$, will be at least four times larger than the second, $\lambda(1 - f)(\Delta_m - \Delta_g)$.

Rearrangement of eq. 7 yields an expression for f, the fraction of carbon buried in organic form:

$$f = \frac{\delta_{ab} - \delta_i - \lambda(\Delta_m - \Delta_g)}{\varepsilon - \Delta_g - \lambda(\Delta_m - \Delta_g)} \tag{8}$$

Commonly (*e. g.*, Hayes *et al.*, 1999), f is estimated from $(\delta_{ab} - \delta_i)/(\delta_{ab} - \delta_{ob})$. This is precisely equivalent to $(\delta_{ab} - \delta_i)/(\varepsilon - \Delta_g)$. The numerator and denominator in that fraction lack the correction terms, $-\lambda(\Delta_m - \Delta_g)$, which are prominent in eq. 8. If $\Delta_m \approx \Delta_g$, as at present, $\lambda(\Delta_m - \Delta_g) = 0$ and the terms are inconsequential, independent of the importance of basalt carbonation. Such cases are summarized graphically in Figure 2a. The vertical line at $\delta_{ab} - \delta_i = 6.5$‰ indicates $\delta_{ab} = 1.5$‰, near earth's observed, long-term average value. The lines correspond (left to right) to $\varepsilon = 22$, 26, 30, and 34‰. The shaded area indicates that, depending on the value of ε, $\delta_{ab} = 1.5$‰ corresponds to $0.2 \leq f \leq 0.32$. This range encompasses the values most frequently noted in previous discussions of the carbon cycle. In particular, $\delta_{ab} - \delta_{ob} = 28$‰, corresponding to $\varepsilon = 30$ and $\Delta_g = 2$‰, is representative of much of the Phanerozoic (Hayes *et al.*, 1999).

The lower *f* values marked by shading in the other frames of Figure 2 correspond to the same value of δ_{ab} but are based on different estimates of Δ_g, Δ_m, and λ. Negative values of Δ_g are observed when sedimentary carbonates are strongly affected by methanogenic diagenesis (Irwin *et al.*, 1977). In Phanerozoic strata, which have formed in the presence of relatively abundant O_2 and SO_4^{2-}, this phenomenon is restricted to concretions or other zones in which supplies of sedimentary organic matter have been large enough that methanogenesis has eventually become prominent. When concentrations of O_2 and SO_4^{2-} in seawater were significantly lower, methanogenesis must have been more important. Accordingly, the effects of negative values of Δ_g, corresponding to globally important levels of methanogenic diagenesis, are explored in Figures 2b and 2c. Figure 2d shows that variations in Δ_m are probably least important in affecting estimates of *f*. Under steady-state conditions, inversion of the oceanic ^{13}C gradient – enrichment of ^{13}C in bottom waters (Δ_m = -5‰, Fig. 2d) – is practically required to produce $\delta_{ab} - \delta_i < 0$.

Redox Balances in the Carbon Cycle

Figure 3 duplicates the plan of Figure 1 but depicts flows of oxidants and reductants generated by the carbon cycle. The biological cycle of production and respiration is at its center. Redox partners for C are generalized as Red and Ox. The focus on *oxidants* rather that *oxygen* is necessary. The carbon-burial flux provides information about the consumption of electron donors but not about the identity of those donors. Over the course of earth history, the electron-donating role of Red has been played by H_2, Fe^{2+}, S^{2-}, and H_2O (at least). Correspondingly, the oxidized forms of these substances have accumulated in earth's crust. The rate of accumulation will be set by the difference between the rate at which carbon-cycling produces oxidants and the rate at which those oxidants are consumed.

To quantify rates, we begin by viewing the J_o terms, introduced above as fluxes of carbon, as fluxes of reducing power. The L terms shown in Figure 3 represent flows of oxidizing or reducing power carried by other elements or by mixtures of C and other elements, (moles O_2 equivalent)/time. Because reduction of CO_2 to organic carbon and oxidation of H_2O to O_2 are both four-electron processes, values of the J_o and L terms are numerically equivalent. Production of one mole of organic carbon could be balanced by oxidation of two moles of H_2, eight moles of Fe^{2+}, 0.5 mole of S^{2-} (to SO_4^{2-}), or two moles of H_2O. All would be equivalent to one mole of O_2. To emphasize that it pertains to the net effect of multiple processes, rather than to a specific flux, we use A_{Ox} to designate the rate at which oxidants accumulate in the crust and exogenic reaction chamber.

To begin, the biological carbon cycle releases oxidants at the rate at which organic carbon is buried in deep sediments (J_{ob}). The rate of accumulation is then moderated by effects of two types. Within the crust itself, a portion of the oxidants is consumed by the geological carbon cycle. Two pathways are shown in Figure 3. The first is oxidative weathering of organic carbon exposed on and eroded from the continents (J_{or}). The second is oxidation of reduced gases produced at subduction zones. The corresponding flux is designated as L_{Redv}. It includes not only volcanic gases (H_2, CO, SO_2) but also products ranging from methane to petroleum which are delivered to the exogenic reaction chamber by thermal processes in subduction zones and deep basins.

The export of oxidants and reductants also moderates A_{ox}. This occurs in subduction zones and at the top of the atmosphere. Within subduction zones, electrons are transferred between subducted organic materials (J_{os}) and oxidants (metal oxides and SO_4^{2-}, L_{Oxs}) in the descending slab. Products will include not only those returned to the crust (noted above) but also unconsumed oxidants (L_{Oxd}) and reduced carbon (diamond, graphite, J_{od}) exported to the mantle. Subduction of carbonate decreases the mass of carbon in the crust but, because carbon is supplied from the mantle as CO_2, does not export either oxidizing or reducing power from the crust. Subduction of sulfide is similarly inconsequential. Mantle S occurs as sulfide even under oxidizing conditions (*e. g.*, ΔFMQ ~ 2; Luth, 2004).

At the top of the atmosphere, H_2 can be lost to space, thus exporting reducing power and effectively increasing A_{Ox}. This occurs when reduced gases of either volcanic or biological origin reach high altitudes. Depending on atmospheric conditions, a portion of the reducing power carried by these gases can be lost as hydrogen escapes to space (Catling *et al.*, 2001).

Summation provides an estimate of the rate at which oxidants will accumulate:

A_{Ox} = (Net release of oxidants within crust by C cycle) + (reductant export) - (net oxidant export)

$$A_{\mathrm{Ox}} \geq (J_{\mathrm{ob}} - J_{\mathrm{or}} - L_{\mathrm{Redv}}) + L_{\mathrm{Redx}} - (L_{\mathrm{Oxd}} - J_{\mathrm{od}}) \qquad (9)$$

The second expression denotes A_{Ox} as a minimum value because the net release of oxidants by the C cycle may exceed $J_{\mathrm{ob}} - J_{\mathrm{or}} - L_{\mathrm{Redv}}$. This would occur if a portion of the organic carbon returning from continents (J_{or}) was not reoxidized but instead simply reburied. The efficiency of reoxidation will depend on the nature of Ox (*e. g.*, O_2 *vs.* SO_4^{2-}) and the reactivity of J_{or} (*e. g.*, graphitic kerogen *vs*. hydrocarbons).

Equation 9 ignores a category of processes often considered in *oxygen* budgets. Sediments and oceanic crust assimilated by continents will incorporate portions of the Red and Ox from the exogenic reaction chamber. Oxidized and reduced forms of sulfur and iron are prime examples. Surging flows of these reactants to the sediments or from continents can, for example, significantly affect levels of O_2 in the atmosphere and ocean. These and related phenomena, especially in the sulfur cycle, have already been elegantly treated by others (Berner, 2004; Canfield, 2004).

Imbalances yielding a net release or consumption of oxidizing power by the carbon cycle are of two types. The more obvious are marked by isotopic signals indicating rapid variations of *f* and consequent departures from steady state. At such times, the system will evolve dynamically (Rothman *et al.*, 2003). At other times, when *f* varies slowly, the system will evolve quasi-statically through a succession of steady states. The persistence of small imbalances between fluxes can lead to the accumulation of crustal inventories of carbon, chiefly on the continents. In this case, the fluxes designated in eq. 9 should be represented as time-dependent variables. Then, at any time, *t*:

$$\int_0^t A_{\mathrm{Ox}}(t)\mathrm{d}t = \int_0^t \left[J_{\mathrm{ob}}(t) - J_{\mathrm{or}}(t) - L_{\mathrm{Redv}}(t)\right]\mathrm{d}t + \int_0^t L_{\mathrm{Redx}}(t)\mathrm{d}t - \int_0^t \left[L_{\mathrm{Oxd}}(t) - J_{\mathrm{od}}(t)\right]\mathrm{d}t \qquad (10)$$

The first term on the right is the integrated difference between burial and reoxidation of organic carbon. It quantifies the accumulation of organic carbon in continents and marine sediments. The second and third terms quantify the effects of loss of H_2 to space and of subduction of oxidized and reduced materials. Notably, this summation of oxidation has no isotopic dimensions. J_{ob} is related to *f* and thus to the isotopic record, but it is $J_{\mathrm{ob}} - J_{\mathrm{or}} - L_{\mathrm{Redv}}$ that matters, and it is further altered by effects of subduction and escape of H_2 to space.

The first term in Equation 10 is closely related to a principles dating from the 19th century (J. J. Ebelmen's work from 1845 to 1855, reviewed by Berner & Maasch, 1996) and elaborated in modern detail most influentially by Garrels (*e. g.*, Garrels & Perry, 1974) and Berner (2004 and earlier references cited therein). Specifically, the amount of organic carbon stored in the crust should balance the oxidizing power represented by the crustal inventories of Fe^{3+}, SO_4^{2-}, and O_2. To this, space science and plate tectonics have added the second and third terms.

It is difficult to reconstruct the histories of the variables in eq. 10. A boundary value for the first integral, however, can be obtained by consideration of crust-mantle carbon budgets and variations in *f*, the organic-carbon burial fraction.

Inputs of Mantle Carbon

Fluxes and inventories throughout the carbon cycle depend on inputs of carbon from the mantle. These occur at mid-ocean ridges, arc volcanoes, hotspots, and in plume events. The present strengths of these sources will be considered sequentially. An estimate of variations over the course of earth history will follow.

Mid-ocean ridges. Each year, 21 km^3 of basalt is added to the oceanic crust at spreading centers [Crisp, 1984; also consistent with a plate-creation rate of 3.4 km^2/yr (Rowley, 2002) and a plate thickness of 5-7 km (Kadko *et al.*, 1994; White *et al.*, 1992)]. Sampled after cooling at the seafloor, its CO_2 content is dependent on the hydrostatic pressure. At the depths of mid-ocean ridges, the result is commonly about 200 ppm (the routinely reported concentrations refer to weights of CO_2). The question is how much CO_2 was in the parent magma. The difference will have been transferred, by way of hydrothermal circulation, to the ocean.

Recently, Saal *et al.* (2002) have shown that, in undegassed MORB (mid-ocean-ridge basalt), concentrations of CO_2 vary with those of Nb. The weight ratio is $CO_2/Nb = 239 \pm 46$ (2σ). Since Nb is not lost during degassing, the initial CO_2 content of a sample of MORB can be estimated from its content of Nb. The average for normal MORBs (*i. e.*, those in which trace-element abundances have not been affected by proximity to plumes or recently subducted continental materials) on the East Pacific Rise is 3.45 ppm Nb (Su & Langmuir, 2003). The estimated, average, initial content of CO_2 is thus $3.45 \times 239 = 825$ ppm. If 200 ppm remain in the cooled basalt, the difference transmitted to the exogenic reservoir is 625 ppm. Given a rock density of 2.8 g/cm^3, this corresponds to 0.8 Tmol C/yr (Tmol = teramol = 10^{12} mol). If the Nb average quoted for all MORBs (5.02 ppm; Su & Langmuir, 2003) is instead used as the basis for the calculation, the result is 1.3 Tmol C/yr. These values bracket a third estimate, namely 0.9 Tmol C/yr, reported in the original publication (Saal *et al.*, 2002) and reached using a slightly different approach.

Numerous alternative estimates have been based on $CO_2/^3He$ ratios in hydrothermal fluids and gases. These have been reviewed by Resing *et al.* (2004), who settle on a range of 0.5 – 2 Tmol C/yr. Preferring the approach based on chemical analyses of the rocks, we adopt 1 Tmol C/yr as the present magnitude of the mid-ocean-ridge component of J_{am}.

Arc volcanoes. The annual magma volume is 0.5 km^3 (Carmichael, 2002). Carbon dioxide is abundant in the gases, but its isotopic composition often deviates from the mantle value and the CO_2 is regarded as deriving from subducted sedimentary carbonates and organic carbon as well from the mantle (Sano & Marty, 1995; Sano & Williams, 1996; Shaw *et al.*, 2003, 2004). The total flux of CO_2 from arc volcanism is ≈ 1.6 Tmol/yr (Hilton *et al.*, 2002). Of this, ≈ 13% is from the mantle (Shaw *et al.*, 2003), yielding an arc-volcanic component of J_{am} of 0.2 Tmol C/yr. The remaining 1.4 Tmol/yr is recycling crustal C. Wallace (2005) obtains a similar result by a different method.

Oceanic Islands and Plumes. In a collection of estimates, this is the most uncertain. The annual volume of magma is approximately 3 km^3 (though possibly as small as 1.9 km^3), combining igneous provinces and hotspot volcanoes on continents with those in the ocean (Crisp, 1984). A more recent, separate tabulation of large igneous provinces by Marty & Tolstikhin (1998) finds a total of 95.5×10^6 km^3 in the past 250 Ma, for a rate of 0.4 km^3/yr. It's broadly agreed that these magmas are volatile-rich compared to MORB. Basing their estimate on ^3He budgets, Marty & Tolstikhin (1998) suggest that the total output from oceanic islands and plumes "is at best similar to that of spreading centers." Given our estimate above, this suggests an input of somewhat less than 1 Tmol C/yr.

Since mid-ocean ridge magmas are roughly 10× more voluminous, the estimated equal flux of mantle CO_2 from oceanic islands and plumes calls for a 10× enrichment of CO_2, and thus perhaps of Nb, in the parent magmas. Observed enrichments of Nb (Hofmann, 2004) range from at least 13× (Mangaia, Pitcairn, Tahaa) to 2× (Mauna Loa). Moreover, Pineau *et al.* (2004) have suggested that CO_2/Nb ratios might range to values more than 3× higher than that found by Saal *et al.* (2002). In sum, the estimate of 1 Tmol C/yr, equal to that at the spreading centers, is plausible but highly uncertain.

Together, mid-ocean ridges, arc volcanoes, and emissions at island volcanoes and during plume events provide an annual input from the mantle of approximately 2.2 Tmol C.

Inventories and Accumulation of Carbon

Total quantities of carbonate carbon in the crust, estimated from stratigraphic inventories (Hunt, 1996; Holser *et al.*, 1988; Wedepohl, 1995; DesMarais, 2001; Berner, 2004; Arvidson *et al*, 2005), commonly range from 2800 to 6500 Emol (Emol = examol = 10^{18} mol). The same reports provide estimates of the total quantity of organic carbon ranging from 675 to 1300 Emol. Only one of these (Arvidson *et al,* 2005) includes carbonate associated with basalt. It also yields the lowest ratio of organic to total carbon, namely 0.13. The other reports yield organic fractions ranging from 0.15 to 0.20 and seem to be influenced by isotopic mass balances which suggest higher relative quantities of organic carbon.

Wilkinson & Walker (1989) took an alternative approach and focused exclusively on sedimentary carbonates. Examining mass-age data, they found that the best fit could be provided by a constant-mass, constant-burial system with first-order recycling and including 9600 Emol carbonate carbon. An alternative fit emphasizing data from younger sequences yielded a result of 7900 Emol. If we arbitrarily adopt an organic-carbon fraction of 0.15, the corresponding inventories of organic carbon are 1700 and 1400 Emol, for total carbon inventories of 11,300 and 9300 Emol.

The most detailed inventory (Holser *et al.*, 1988) provides total crustal C = 7640 Emol. Favoring the approach using mass-age data, particularly that based on younger sequences, we weight it equally with the stratigraphic compilations and estimate total crustal C = 8500 Emol.

The time required to accumulate this inventory depends on assumptions about the input flux. If the total flux of 2.2 Tmol C/yr estimated above were constant, the time required would be 3.86 billion years. More commonly, it's believed that, earlier in earth history, such fluxes were higher. Here, we follow Sleep & Zahnle (2001) and Lowell & Keller (2003). These authors scale input fluxes to estimates of high-temperature heat flow, chiefly at spreading centers. For the case in which continents grew episodically from 10 to 80% of current area between 3200 and 2500 Ma, high-temperature heat flow is calculated to decrease from 9× the current level at 3800 Ma, to 4.9× at 3200 Ma, to 2.3× at 2500 Ma, and then to decline exponentially. The resulting scaled carbon flux is shown in Figure 4.

Integration of that flux beginning at 3800 Ma, the end of the late, heavy bombardment, yields the totals depicted graphically in Figure 5. The sum exceeds 8500 Emol, the estimated present crustal inventory, after only 575 Myr, at 3225 Ma. In fact, with continents just beginning to form and crustal storage reservoirs thus sharply restricted, returns of carbon to the mantle would probably have become nearly equal to inputs from the mantle well before then.

Together, Fig. 5 and eqs 1-10 provide a new context for considering the development of the carbon cycle. Before turning to the isotopic records, however, we must first review available information regarding the fates of carbon in subduction zones.

Carbon Cycling at Subduction Zones

Processes in subduction zones are crucial to redox balances in the carbon cycle. Figure 6 shows flows of carbon (in oxidized and reduced form) and other products of carbon cycling into, through, and out of subduction zones. Reducing power produced by the carbon cycle is carried into subduction zones by organic carbon (J_{os}). Oxidizing power is carried by sulfate and by ferric iron. The crossing paths and redox reactions suggest the diverse transformations involved. While many different sequences of reactions are possible, the equations in Figure 6 summarize the required balances of mass and electrons. All of the carbon that enters the subduction zone must be transferred in some form to either the crust or mantle. And the balance between inputs of reductants and oxidants must be reflected by materials leaving the subduction zone. Resolution and dissection of processes within subduction zones is not currently possible, but available evidence bears on two key questions. When a slab is subducted, (1) what happens to the carbon and (2) what happens to the reducing power carried by the organic matter?

Carbon fluxes. The downgoing flux, ($J_{ad} + J_{od}$), might be quantified directly if we knew how much material was being incorporated by the mantle and if samples of it were returned to the surface so that their carbon contents could be determined. Although J_{od} and J_{ad} are sampled by diamond-bearing rocks and mantle xenoliths, it is not clear how representative these samples are, nor do they allow for quantification of the total downgoing C flux.

More headway can be made by considering the fluxes from arc volcanism and other volatile emissions from subduction zones and then estimating the downgoing flux from the difference between the trench input and surface output. The magnitudes of both are rather uncertain; here we summarize the best estimates. The three inputs are the organic and carbonate components of subducted sediment (J_{os} and J_{as}) and the carbonated basalt in the subducting crust (J_{az}). The global subducting-sediment budget of Plank & Langmuir (1998) puts J_{as} at 0.9 Tmol C/yr. Estimates of J_{os} are very poorly constrained, mostly because it's small in comparison to fluxes to and from the continents and shelves. For the modern C cycle, Holser *et al.* (1988) estimate $J_{oc}/J_{os} \approx 40$. We adopt their value, $J_{os} = 0.2$ Tmol C/yr, suggesting a mean C_{org} content for subducting sediment of 0.13 wt%.

The third flux, J_{az}, likely delivers most of the carbon to subduction zones. It derives from J_{aw}, for which estimates range over more than an order of magnitude from less than 1 to more than 3 Tmol C/yr

(Bach *et al.*, 2003). The alternate fate for carbon buried by basalt carbonation is represented by J_{ah}, the portion of carbonated basalt actually accreted onto continents. Since this is relatively small, it follows that carbonate can be stored in ocean crust along passive margins for hundreds of millions of years, as in much of the Atlantic basin today. The idea that J_{az} approaches J_{aw} incorporates an assumption that, following tectonic rearrangements, such material is eventually subducted. The resulting rough estimate of the total subduction input is 2-4 Tmol C/yr.

For the volatile outputs from arcs, the most complete budget has been compiled by Hilton *et al.* (2002), who considered subduction inputs to and volatile emissions from 26 arc systems worldwide. The authors calculated a global volcanic arc CO_2 flux of 1.6 Tmol C/yr and emphasized the importance of distinguishing between sources of volatiles. For CO_2 these are carbonate and organic C in the subducting slab and CO_2 in the mantle wedge. Since the mantle component amounts to 0.2 Tmol C/yr (noted above), j_{vCO2} = 1.4 Tmol C/yr. The portion due to subducted carbonates can be estimated from the isotopic composition of the non-mantle component. For all of the arcs it exceeded the input of sedimentary carbonate. In all cases but one, inclusion of carbonated basalt eliminated the shortfall. Notably, these results are at odds with calculated phase equilibria that indicate carbonated basalts should undergo little devolatilization along most subduction geotherms (Kerrick & Connolly, 2001). The other component of J_{av} is j_{sCO2}, emission of CO_2 from seeps, especially in fore-arc and back-arc regions. This flux is unconstrained, and may be as large as j_{vCO2} (Hilton *et al.*, 2002). Ingebritsen and Manning (2002) have pointed to diffuse fluid flow through tectonically active crust as potentially a major flux of subduction-derived volatiles. This degassing pathway may be sufficient to reconcile the crust-mantle water balance, and could well constitute a significant return of slab-derived CO_2 to the crust. Accordingly, J_{av} is between 1.4 and 2.8 Tmol C/yr.

The other return flux of carbon from subduction zones to the exogenic chamber is J_{ov}, the reduced carbon from high- and low-temperature seeps, primarily CH_4. The related geological forms are diverse, and include mud volcanoes and seeps associated with gas hydrates (Milkov & Etiope, 2005; Milkov, 2005). Their output of CH_4, estimated at 2.1 Tmol/yr (Milkov & Etiope, 2005), derives from microbial methanogenesis and thermal processes in sediments and sedimentary rocks as well as from subducted carbon. Since the carbon in J_{ov} (= CH_4) has oxidation number = -4 and the organic carbon in J_{os} has oxidation number = 0, redox balance provides the stronger constraint. If J_{os} is approximately 0.2 Tmol C/yr, J_{ov} cannot be larger than 0.1 Tmol C/yr. Total volcanic and seep fluxes of carbon ($J_{\mathrm{av}} + J_{\mathrm{ov}}$) are between 1.5 and 2.9 Tmol C/yr.

From inputs of 2-4 Tmol C/yr and recycling fluxes of 1.5-2.9 Tmol C/yr, we estimate that the fraction recycled is ≈ 0.6. By difference, the flux returning to the mantle is 0.8-1.6 Tmol C/yr.

Reducing power. Any reduced C sent to the mantle – graphite, diamond, elemental C – leaves oxidant behind in the surface environment, thus contributing to A_{Ox}. It's also possible that organic C would be oxidized within the subduction zone by reaction with sulfate or an oxidized metal such as Fe^{3+}. When this occurs, does the reduction product (Fe^{2+}, for example) become an organic-carbon proxy that also contributes to A_{Ox}? No, the reaction instead amounts to a last-minute reversal of processes within the carbon cycle. Within the exogenic reaction chamber, Fe^{3+} will have been produced within the downgoing slab by hydrothermal alteration and by oxidation of Fe^{2+} at the expense of O_2. Or the sulfate will have been produced by processes within the carbon cycle. In either case, the oxidizing power will be represented by an equivalent quantity of organic carbon. For the carbon cycle, therefore, the oxidation of organic carbon by oxidized metals or sulfur within subduction zones is a functional equivalent of biological respiration. Details follow.

If the Fe^{3+} or sulfate is a product of aerobic oxidation, it carries the oxidizing power of O_2 produced during photosynthesis. The same organism that produced the O_2 produced an equivalent amount of organic carbon. The oxidation of that organic material within the subduction zone amounts to a reversal of the overall process.

If the Fe^{3+} was produced at the expense of sulfate during hydrothermal alteration, that sulfate can similarly be traced to photosynthetic O_2 and carbon. The chain of chemical events has an additional link, but the oxidation of organic carbon within the subduction zone is again simply a reversal of the process.

If the sulfate was produced by anaerobic, photosynthetic bacteria, those organisms will have produced an equivalent amount of organic carbon. The oxidation of that organic material within the subduction zone amounts to a reversal of the overall process.

Finally, if the Fe^{3+} was produced by serpentinization, an equivalent quantity of H_2 will also have been produced and used by microbiota to produce an equivalent amount of organic carbon, either directly, through chemosynthesis, or indirectly, through consumption of O_2, photosynthetic production of organic matter, *etc.* Again, the oxidation of organic C within the subduction zone amounts simply to a reversal.

If the subducted organic carbon returned to the surface as CO_2 after reducing an inorganic substance to some oxidation state lower than that of its input – if $Fe^{3+}/\Sigma Fe$ in the downgoing slab were driven to values lower than $Fe^{3+}/\Sigma Fe$ in unaltered MORB – *that* would contribute to A_{Ox}. Failing that, $J_{od} > 0$ provides the only route by which processes in subduction zone can yield a net export of oxidizing power by the carbon cycle.

In magnitude, J_{od} is constrained to be less than J_{os}. Exchange of C between reduced and oxidized pools is not excluded. Some of the C in J_{od} might derive from J_{as} or J_{az}. Estimation of J_{od} requires knowledge of J_{os} and L_{Redv}. The rate of subduction of organic matter, as discussed above, is here taken as 0.2 Tmol/yr, though better estimates are clearly warranted. L_{Redv} has two components: the reduced gas flux from arc volcanoes, represented in Figure 6 by j_{H2}, and the reduced gases from other seeps, represented by j_{CH4}.

The reduced component of the volcanic gas flux is represented by j_{H2+SO2} and j_{H2S}. In the present context, the question is how it relates to J_{os}, the reducing power delivered by subduction of organic carbon. The hydrogen abundance in volcanic gases is set by redox equilibrium with water, such that H_2/H_2O ratios are maintained near ~0.01 at most eruptive temperatures (Giggenbach, 1996). Taking the arc magmatic-water flux at 17 Tmol/yr (Wallace, 2005) results in a hydrogen component of 0.17 Tmol/yr. The SO_2 efflux from arcs, some of which may derive from sources other than reduction of subducted sulfate, is of similar magnitude, 0.16-0.28 Tmol/yr (Halmer *et al.*, 2002; Wallace, 2005). Other reduced species in arc gases are relatively minor. The ratio of H_2S to SO_2 is generally between 1 and 0.05 (Halmer *et al.*, 2002), and some of the hydrogen sulfide released at volcanic arcs likely derives from volatilization of sulfide in the downgoing slab rather than reduction of sulfate by organic carbon. The reducing power carried by other volatiles such as CO, COS, and CS_2 is orders of magnitude lower. Since H_2 and SO_2 represent two-electron reductions, the total flux is halved to convert to moles O_2 equivalent whereas H_2S produced from sulfate represents eight electrons or two mol O_2 equivalent. The resulting estimate from gas chemistry is 0.2 Tmol O_2 equivalent/yr from H_2 and SO_2 and 0.4 to 0.02 Tmol O_2 equivalent/yr from H_2S. By itself, the flux of H_2 and SO_2 is already equivalent to the reducing power carried by subducted organic carbon. The obvious presence of additional reduced outputs, namely volcanic H_2S and hydrocarbons at seeps (j_{CH4}) shows that better knowledge of redox budgets for subduction zones is needed. With due regard for the uncertainties imposed by the present budgets, it also *suggests* that most or all reducing power carried by subducted organic carbon is returned to the exogenic reaction chamber and that J_{od} is small at present.

Cycling of Carbon and its Redox Partners Over Time

Over time, the crust has accumulated carbon. Integrated inputs from the mantle have exceeded integrated returns to the mantle. As a means of exploring the balance, we can accept the fluxes and reservoirs proposed thus far as hypotheses and consider how 8500 Emol C might have accumulated and what electron donors were probably associated with the production of organic carbon.

The crust-mantle carbon balance. Values of $(J_{ad} + J_{od})/J_{am}$ control the accumulation of crustal C. When they are less than 1, the crustal inventory will grow. Ideally, a geologic record would exist, but proxies for $(J_{ad} + J_{od})$ are rare. The low $\delta^{13}C$ values of some diamonds, particularly those of eclogite paragenesis, strongly suggest derivation from crustal organic carbon (Pearson *et al.*, 2004), though this has been disputed (Deines *et al.*, 2001). Recently, it's been suggested that organic carbon can be subducted beyond 250 km and contribute to sublithospheric diamonds (Tappert *et al.*, 2005). The stability of carbonated eclogite at high pressures and temperatures (Dasgupta *et al.*, 2004) indicates that eclogitization may be an important route for the subduction of carbon (both oxidized and reduced) into the mantle. This is particularly interesting in light of recent suggestions that eclogitization is a geologically recent phenomenon (Bjørnerud & Austrheim, 2004). A hotter upper mantle earlier in earth history would more efficiently devolatilize downgoing slabs at shallower depths, removing both carbon and water. Shallow decarbonation, combined with drying of the slab and consequent inhibition of the formation of eclogite, may have meant that J_{od} and J_{ad} were small early in Earth history (DesMarais, 1985). Much depends on the tectonic regime, and when the present style of plate tectonics began, which has been the subject of much debate (Van Kranendonk, 2004; Stern, 2005).

One view takes the slow growth of continents together with the steep early declines in the rate at which carbon is delivered from the mantle (Fig. 4) as constraining variations in $(J_{ad} + J_{od})/J_{am}$ quite strongly. The scenario associated with Fig. 4 provides 80% of the present continental area by 2.5 Ga. By comparison, Veizer & Mackenzie (2004) point to evidence suggesting that only 25% of continental crust accumulated between 4.0 and 2.6 Ga, another 35% in the interval to 1.7 Ga, and the final 40% thereafter. Because the continents house the major reservoirs of crustal carbon, $(J_{ad} + J_{od})/J_{am}$ must approach 1 (no net crustal storage) in the early Archean and decline to lower values only as continents grow. The time course of $(J_{ad} + J_{od})/J_{am}$ shown in Figure 7a fits these criteria while eventually yielding a crustal inventory of 8500 Emol C (Fig. 7b) and a modern $(J_{ad} + J_{od})/J_{am} = 0.55$. The latter value is in the middle of the range estimated above (0.36 - 0.73).

The accumulation of organic carbon and oxidized electron donors. Reconstruction of redox budgets requires estimates of *f*. These derive from interpretation of the carbon isotopic records, with due attention to the possible importance of Δ_m, Δ_g, and λ. Figure 8 summarizes observations of δ_{ab} and δ_{ob}.

The latter represent chemically isolated samples of kerogen (Strauss & Moore, 1992). The ratios of H/C in Precambrian kerogens are frequently well below 0.5 (Hayes *et al.*, 1983). Accordingly, the kerogens have been extensively dehydrogenated by processes that frequently involve the loss of ^{13}C-depleted hydrocarbons and thus enrichment of ^{13}C in the residual kerogen. Because our objective is to reconstruct probable isotopic compositions of organic carbon at the time it was removed from the exogenic reaction chamber (that is, as it flowed through the arrow representing J_{ob} in Fig. 1), we will base our estimates of f mainly on the lower values of δ_{ob} in each time interval.

4400 - 3800 Ma. In parallel with the isotopic records summarized in Figure 8, the integrations in Figures 5 and 7 have begun at 3800 Ma. This point in time roughly marks the end of the late, heavy bombardment and the beginning of earth's sedimentary record. Catling *et al.* (2001) have considered how earlier events might have set the stage for carbon cycling. In particular, they estimate that impacts of asteroids between 4400 and 3800 Ma probably delivered 1000 Emol of reduced carbon to earth's surface. To whatever extent such material was not incorporated by the mantle, earth's crust will have begun with an inventory of primordial organic carbon. When biological cycling of carbon began, the processes would have been

Production: $(CO_2)_{\text{From Outgassing}} + \text{Red} \rightarrow (C_{org})_{\text{From Production}} + \text{Ox}$

Recycling: $(C_{org})_{\text{Primordial}} + \text{Ox} \rightarrow (CO_2)_{\text{Crustal}} + \text{Red}$

Net: $(CO_2)_{\text{From Outgassing}} + (C_{org})_{\text{Primordial}} \rightarrow (C_{org})_{\text{From Production}} + (CO_2)_{\text{Crustal}}$

In these equations, Red and Ox are reduced and oxidized forms of a redox partner such as Fe or S. Reactions between surviving, asteroidal organic material (termed "Primordial") and oxidants produced during carbon cycling might have been biologically catalyzed and occurred within the exogenic reaction chamber or they might have been thermal and occurred only at depth within accumulating sediments. In either case, the resulting CO_2 became part of the crustal inventory. Such reactions would have two effects: (*i*) an exchange of biotic organic carbon for primordial organic carbon, and (*ii*) consumption of oxidants. Only when production acted to increase the inventory of C_{org} (here taken to begin at 3.8 Ga) would oxidants begin to accumulate.

3800 - 2800 Ma. For this interval, the isotopic record of sedimentary carbonates compiled by Shields & Veizer (2002) includes 24 stratigraphic units. With an average value of δ_{ab} = -0.1‰, they are consistently enriched in ^{13}C relative to mantle carbon. The standard deviation of the population is 1.9‰. For the same interval, Figure 8 yields an estimate of δ_{ob} = -36‰. Nakamura & Kato (2004) measured values of δ_{aw} in basalts from the Warrawoona Group (3425 Ma, Western Australia). Their average result, -0.3 ± 1.2‰, does not differ significantly from δ_{ab} in sedimentary carbonates in this time interval. Accordingly, $\Delta_m \approx \Delta_g$, the $\lambda(\Delta_m - \Delta_g)$ terms in eq. 8 are small, and $f = (\delta_{ab} - \delta_i)/(\varepsilon - \Delta_g) = (\delta_{ab} - \delta_i)/(\delta_{ab} - \delta_{ob}) = 0.14$. Observed values of δ_{ab} and δ_{ob} then indicate that 14% of the carbon being delivered to the exogenic reaction chamber by outgassing of CO_2 from the mantle was being buried as reduced, organic carbon.

The net production of organic carbon during any increment of time can be estimated:

$$\text{Net } C_{org} = (C_{org} \text{ produced by reduction of } J_{am}) + (C_{org} \text{ produced by reduction of recycling C}) - (C_{org} \text{ oxidized during recycling}) \quad (11)$$

The recycling carbon (*i. e.*, $J_{\mathrm{or}} + J_{\mathrm{ar}} + J_{\mathrm{ov}} + J_{\mathrm{av}}$) will be some portion of the total crustal carbon. If a representative half-mass age is taken as 300 Myr, the fraction recycling in a 10-Myr interval will be 2.3% (see Table 1). In any 10-Myr interval, therefore, 2.3% of crustal carbon will be recycled, essentially mixing with the 10-Myr input of mantle carbon. Of that total, a portion controlled by $(J_{\mathrm{ad}} + J_{\mathrm{od}})/J_{\mathrm{am}}$ will be returned to the mantle. Of the remainder, a fraction f will be buried in organic form. Assuming that all recycling organic carbon is oxidized, an integrable form of eq. 11 is then:

$$\text{Net C}_{\mathrm{org}} = f\left[J_{\mathrm{am}}\tau\left(1-\frac{J_{\mathrm{ad}}+J_{\mathrm{od}}}{J_{\mathrm{am}}}\right)+\gamma M\right]-\gamma M_{\mathrm{o}} \qquad (12)$$

where γ is the fraction of crustal carbon recycling in a time interval of length τ (*e. g.*, 0.023 for $\tau = 10^7$ yr and a half-mass age of 300 Myr) and, at the beginning of the time step, M is the total crustal inventory of carbon in all forms (Fig. 7b) and M_{o} is the total inventory of organic carbon. Stepwise summation provides an estimate of the integrated production of organic carbon, the first integral on the right side of eq. 10.

The calculation is based on (1) values of $(J_{\mathrm{ad}} + J_{\mathrm{od}})/J_{\mathrm{am}}$ chosen to provide the observed crustal inventory of C (Fig. 7a); (2) values of J_{am} provided by Fig. 4; and (3) values of f shown in Figure 9a and estimated from the observations summarized in Fig. 8. Setting $M = M_{\mathrm{o}} = 0$ at 3800 Ma and summing Net $\mathrm{C}_{\mathrm{org}}$ yields the result shown in Figure 9b. Because a sharp drop in δ_{ob} suggests a major change in carbon cycling at approximately 2770 Ma (Hayes, 1983, 1994), we will focus first on the interval 3800 - 2800 Ma. By 2800 Ma, M_{o} = Oxidant release = 300 Emol O_2 equiv.

To place this result in context, consider the inventories summarized in Table 2. For all of the materials considered, a range of estimates can be found in the literature. Those included here are representative high and low values. The value of 300 Emol O_2 equiv. greatly exceeds the oxidizing power represented by O_2 in the modern atmosphere and ocean and approaches the low estimate of the amount of oxidizing power represented by total crustal deposits of sulfate and sulfate dissolved in seawater. These comparisons decisively eliminate two otherwise-interesting possibilities, namely that O or S could have served as the dominant redox partner for C at this stage of earth history. In the first case, levels of O_2 would have risen high enough to inhibit the mass-independent fractionation of sulfur isotopes. In the second, concentrations of dissolved sulfate would have climbed to levels that lead to large differences between the ^{34}S contents of sedimentary sulfides and sulfates, a signal that is not observed until later (Hayes *et al.*, 1992).

The remaining oxidized product listed in Table 2 is ferric iron. Its crustal inventory is large enough to offer plenty of headroom. Iron formations are, moreover, important components of the Archean sedimentary record. The present context, however, requires that iron served as the electron donor in primary production while the environment remained strictly anaerobic. An organism capable of utilizing Fe^{2+} directly has recently been isolated (Jiao *et al.*, 2005). In principle, we need look no farther, but alternatives deserve consideration. These are: (*a*) the true value of f was really near zero; (*b*) f was 0.14 but no oxidants accumulated; or (*c*) f was 0.14 and the electron donor was H_2, for which the immediate oxidized product (H_2O) was invisible, although iron was probably the ultimate source of the electrons.

The true value of f could be approximately zero if the basalt-carbonation correction had been wrongly excluded and the correct value of $\lambda(\Delta_{\mathrm{m}} - \Delta_{\mathrm{g}})$ was 4.9‰. If λ were 0.9, this would require that the initial average value of δ_{aw} had been -5.5‰ and that Nakamura & Kato (2004) found instead -0.3‰ because the isotopic compositions of all of their samples had been affected by post-depositional carbon-isotopic exchange. However, among 42 samples of four different types, the most negative value of δ_{aw} is -3.4‰ and there is no correlation between δ and the abundance of carbonate. Evidence for the required alteration is therefore lacking, making it likely that f truly approached 0.14.

If f approached 0.14 but no oxidants accumulated (*b*, above), $(J_{ad} + J_{od})/J_{am}$ must have been 1, indicating rapid and quantitative return of all carbon to the mantle, even as 3.5 million km^2 of continental crust (Lowe, 1992) formed prior to 3.2 Ga. Moreover, as substantial quantities of organic carbon were forming as required by $f = 0.14$ (and thus $J_{ob}/J_{am} \geq 0.14$), the putatively non-accumulating oxidant, which could not be either O_2 or sulfate and which had to be present only at trace levels, was able to reoxidize all of the organic material completely even as the carbon itself returned quantitatively to the mantle. The required combination of circumstances is practically impossible.

The third alternative, in which f was approximately 0.14 and H_2 served as the electron donor, fits well with multiple lines of evidence. Anaerobic organisms capable of producing organic material from CO_2 and H_2 are abundant and include both chemoautotrophs (methanogens, acetogens) and photoautotrophs (photosynthetic bacteria; Tice & Lowe, 2004, have already postulated that such organisms were important members of near-shore microbial communities 3.4 Ga ago). The potential versatility of microbial ecosystems based on such organisms is great enough to provide both producer and consumer assemblages and thus to stabilize carbon cycling and yield globally consistent isotopic fractionations. Fermentative consumption would remobilize organic C as a mixture of CO_2 and CH_4, providing needed greenhouse warming (Kasting & Catling, 2003) and setting the stage for the isotopic transient observed at 2.8-2.7 Ga (Hayes, 1994).

The required net input of H_2 would be 600 Emol (= 300 Emol O_2 equiv.). Because of the postulated declines in J_{am} (Fig. 4) and increases in $[1 - (J_{ad} + J_{od})/J_{am}]$ (eq. 12), the required rate would rise only slowly from 0.5 Tmol/yr at 3500 Ma to 0.9 Tmol/yr at 2800 Ma. If, as is likely, conditions at the seafloor favored serpentinization reactions (Sleep *et al.*, 2004), a flux of 0.7 Tmol H_2/yr could be provided by alteration of less than 10^{15} g Mg-rich (komatiitic) basalt per year. The present rate of generation of ocean crust is about 6×10^{16} g/yr, so the requirement poses no problem. In the overall sequence of electron transfers, it is only the immediate oxidized product of carbon fixation (H_2O) which is "invisible." The reducing power represented by the organic matter is balanced by Fe^{3+}, which *is* accumulating or being subducted.

To summarize, from both geological and biological points of view, there are highly plausible mechanisms by which substantial amounts of organic carbon could be produced and buried in accord with the isotopic records, with complementary releases of oxidizing power, without any requirement for generation of O_2 during the interval 3800 - 2800 Ga. The most likely redox partner for C during this interval is Fe, either directly *via* phototrophic oxidation of dissolved Fe^{2+}, and/or indirectly, with H_2 shuttling electrons from Fe^{2+} in seafloor basalts to phototrophic and chemoautotrophic producers.

2800 - 1800 Ma. The next billion years begins with the apparent onset of oxygenic photosynthesis (Hayes, 1983, 1994; Summons *et al.*, 1999), includes a period during which the abundance of ^{13}C in sedimentary carbonates was sometimes markedly enriched (Karhu & Holland, 1996; Melezhik *et al.*, 1999), and ends with the likely onset of sulfidic conditions in the deep sea (Canfield, 1998).

Estimates of *f* derived from the isotopic records provide scant evidence that the development of oxygenic photosynthesis, for all its magnificence as a biochemical innovation, provided a significant increase in the net release of oxidizing power. If anything, J_{ob} initially declined, a feature marked by the notch visible at 2.8 Ga in Figure 9a. By 2500 Ma, *f* appears to have risen to 0.16, a value only slightly higher than that estimated for the early Archean. At 2450 Ma, when traces of O_2 quench the mass-independent fractionation of sulfur isotopes, the estimated minimal total release of oxidizing power by the C cycle is 460 Emol O_2 equiv. Although uncertainties in that total are very large, it is far short of the capacities of crustal Fe and S to supply electrons (Table 2). Levels of O_2 in the environment would have been sharply limited by the strength of those sinks.

What, then, happened between 2400 and 2000 Ma? Contents of ^{13}C in carbonates are frequently elevated, occasionally exceeding +10‰ (Fig. 8). Accepting these compositions as representative of the global pool of oceanic dissolved inorganic carbon (DIC) would imply a near-trebling of *f*. Writing three years after Karhu & Holland (1996) published “Carbon isotopes and the rise of atmospheric oxygen,” Melezhik *et al.* (1999) drew on additional data to define three apparently separate pulses of isotopic enrichment. That dissection of the record yields the three spikes in *f* that are represented by broken lines in Figure 9a (alternative stratigraphic correlations yield only two spikes; Bekker *et al.*, 2003). The isotopic signal has been associated with other lines of geochemical evidence indicating that the atmosphere became more oxidizing at about the same time. The ensemble has become known as “The Great Oxidation Event” (Holland, 2002).

One view of the scale of the event is provided by the broken line in Figure 9b. If the isotopic signals represent pulses of carbon burial, the integrated production of organic carbon by 2000 Ma would be 600 Emol greater. As shown by Table 2, that’s more than enough to provide the present inventories of SO_4^{2-} and O_2. But there are problems with interpreting these isotopic variations in terms of carbon burial:

1. There is no parallel isotopic enrichment in the organic carbon, as would be expected if the carbonate represented the oceanic DIC that was the carbon source for primary producers. Karhu & Holland (1996) searched for a signal in the organic-carbon record and found its absence “rather odd.” If the record were not so fragmentary and noisy (preservation is a much greater problem for organic carbon than for carbonate minerals) that the problem could be set aside (Melezhik *et al.*, 1999), this alone would be fatal to the interpretation.
2. Evidence is lacking for the large deposits of organic carbon that should have formed (Melezhik *et al.*, 1999; Aharon, 2005).
3. The sequence of isotopic signals is reversed from that expected. If the oxygenation that cut off mass-independent fractionation of sulfur isotopes was due to an organic-carbon-burial event, the disappearance of the mass-independent fractionation of sulfur isotopes should not precede the first carbon-isotopic enrichments.
4. It is difficult to envision supplies of nutrients great enough to sustain the levels of productivity required to supply the organic carbon. Aharon (2005) has discussed supplies of phosphate very insightfully, concluding that efficient stripping of P from organic matter prior to burial provides the only solution. To achieve the projected values of *f*, the C/P ratio in buried organic matter would have to be 4000 and the organic-preservation rate would have to be 6.6%, about five-fold higher than that observed in the Black Sea.

5. Stratigraphic correlations are not secure enough to demonstrate that the various isotopic excursions are coeval and thus necessarily linked to variations in a global reservoir (Aharon, 2005).
6. Most of the units displaying the isotopic enrichments are dolostones with substantial isotopic variability. In their list of 12 "major localities," Melezhik *et al.* (1999) report within-unit ranges of 3 to 13‰ and an average range of 7‰. Consistent with this, for the interval 2350 to 2000 Ma (inclusive), Shields and Veizer (2002) report 589 δ values between -2.5 and +2.5‰ and 424 between +5 and +13‰. That is, "normal" isotopic abundances are more common than elevated abundances.
7. When complete chemical analyses of the carbonates are reported, they often include substantial concentrations of SiO_2 (to 40%; Melezhik *et al.*, 1999). Stratigraphic columns indicate that some of the isotopically enriched carbonates are closely interbedded with shales (Buick *et al.*, 1998), others are described as "nodular" (Bekker *et al.*, 2003).

The latter features (6 and 7) are more characteristic of diagenetic carbonates than of marine limestones faithfully carrying records of oceanic DIC. When it's recalled that values of $^{13}\delta$ to +13‰ are common in much younger dolomites that have been affected by methanogenic diagenesis (Klein *et al.*, 1999; Mazzullo, 2000), that alternative interpretation demands attention. In fact, attribution of the isotopic signals to methanogenic diagenesis has already been favored by several sets of authors (Yudovich *et al.*, 1991; Dix *et al.*, 1995).

In all likelihood, the diagenetic alternative has failed to win popularity because an alternative does not appear to be needed. Multiple, convergent lines of evidence – independent of carbon-isotopic signals – indicate that thresholds of environmental oxidation were crossed during this time interval (Bekker *et al.*, 2004). When the carbon-isotopic record fits into this picture at least roughly, why not include it? Even more to the point, given the apparent reality of the oxidation, how else should the carbon-isotopic enrichments be explained? They are temporally associated, dramatic and numerous (Bekker *et al.*, 2003), globally distributed, and have the right polarity (enrichment rather than depletion).

Mechanisms of oxygenation. The problem lies not in accepting the isotopic signals as markers of the oxidation but in assuming that they represent the *cause*. This is a key distinction. Either the steady functioning of the carbon cycle catalyzed biological and ecological developments that shifted the relative strengths of oxygen sources and sinks (Holland, 1978) or dramatic changes in carbon fluxes were required. If the former, the carbon-isotopic enrichments are environmental reporters comparable to the mass-independent fractionations of sulfur isotopes. If the latter, they point to increased burial of organic carbon but not necessarily to permanent changes in oxidation.

Flux-driven changes are subject to reversal. Buried organic material will be recycled by erosion and volcanism. As indicated by the downward trend of the broken line in Fig. 9b after 2000 Ma, oxidants will be consumed. Even if a rise in O_2 were driven by increases in J_{ob}, some additional change would be required to stabilize the transition and make it permanent. Geophysical phenomena such as rifting and increased sedimentation can increase J_{ob} but are inherently cyclical. What they accomplish in one epoch will be undone in another. Increased burial of organic carbon is a half answer. It can push O_2 levels higher, but maintaining them will require some further change, a second half to the answer.

Unidirectional change, a permanent strengthening of the source of oxidants, is in the realm of evolutionary biology. Physiological and ecological changes could stabilize higher levels of O_2. Do they serve as the second half of the answer? If so, they are the biological results of geophysical stimuli and we need an explanation for the linkage. Or are physiological and ecological changes answers in themselves? If so, advances in oxygenation have largely biological origins and combinations of disparate phenomena are not required.

Kinetic factors are also pertinent. In discussing the carbon cycle, it's common to distinguish between the *fast*, biological cycle of photosynthesis and respiration and the *slow*, geological cycle in which erosion, weathering, and volcanism are balanced by carbon burial. In global chemical terms, O_2 is a highly reactive, transient intermediate that's produced and consumed within the exogenic reaction chamber. Its steady-state abundance must depend on the relative strengths of sources and sinks in that system. In contrast, sedimentary carbonates and organic materials are outputs from that system. Their relative abundances are controlled by geophysical factors that vary over relatively long time scales.

Causes of the carbon-isotopic transient. We can suggest a sequence of biologically driven environmental changes, associated with a rise in levels of O_2, that would produce the observed isotopic signals without requiring enhanced burial of organic carbon. They would also account for the absence of congruent variations in the organic-carbon isotopic record.

Especially prior to 2.3 Ga, methanogenic diagenesis must have been common. If electrons for biosynthesis were supplied mainly by Fe^{2+}, the insolubility of the oxidized product, Fe^{3+}, meant that electron acceptors were rare in most surface environments (Walker, 1987). When respiring heterotrophs are excluded, the recycling of organic carbon in microbial communities will be managed by fermenters, with methanogens playing a vital role. This will have occurred in the same zones that are now occupied by aerobes. These methanogenic communities will have exchanged CO_2 freely and directly with the oceanic water column and, as a result, the isotopically enriched pools of CO_2 that are characteristic of methanogenic diagenesis in modern environments will not have developed. This situation is summarized in the "before" segment of Figure 10.

The development of oxygenic photosynthesis by at least 2700 Ma began to change that situation, however slowly. Particularly near oxygen-producing communities (many of the isotopically enriched dolostones are associated with stromatolites; Melezhik *et al.*, 1999), methanogens will eventually have been pushed to deeper levels in the sediment. When this occurred, apparently beginning at about 2400 Ma, isotopically enriched pools of porewater DIC will have developed. As carbon was exchanged with the carbonate minerals in the sediment (a process catalyzed by the organic acids produced during fermentation), the isotopic signal characteristic of methanogenesis will have been recorded for the first time. Within about 400 Myr, a second event shut the signal off. Fundamentally, it must have been some weakening of the supply of organic material to methanogenic communities. As suggested in the "after" segment of Figure 10, it could have been caused by a further rise in the availability of electron acceptors. Alternatively, the tight association between stromatolitic producers and methanogenic consumers, indicated by many of the ^{13}C-enriched sequences, might have been destabilized by environmental changes.

As in the Neoproterozoic, the isotopic excursions are associated with apparently extreme glaciations (Young *et al.*, 2001; Tajika, 2003). The effects of those glaciations on global redox geochemistry, if any, are unclear. It has conversely been proposed that the glaciations were caused by global oxidation which destroyed a methane greenhouse *and* that this occurred promptly after the development of oxygenic photosynthesis (Kopp *et al.*, 2005). The second part of this doesn't fit with biomarker records that place the advent of oxygenic photosynthesis at or before 2.7 Ga (Summons *et al.*, 1999; Brocks *et al.*, 2003; Eigenbrode, 2004). It also doesn't fit with the inescapably slow effects of carbon cycling. Releases of oxidizing power have been continuous (Fig. 9b). But the oxidized products accumulated by 2.5 Ga cannot have accounted for more than a fraction of the inventory of ferric iron and almost none of the sulfate (*cf.* Table 2). In those circumstances, by what mechanism did the development of oxygenic photosynthesis *promptly* sustain steady-state concentrations of O_2 high enough to destroy the methane greenhouse? Until that question can be answered, the evidence for (1) a 400-Ma delay between the evolutionary event and its environmental impact and (2) the continuing capacity of Fe and S as redox buffers should overrule speculation.

Oxidation of S by O_2 would have produced sulfate in surface environments. However, by 1800 Ma, the estimated integrated release of oxidizing power (Fig. 9b) was only 820 Emol O_2 equiv. This is still well below the low estimate of the amount required to build the crustal inventory of Fe^{3+} (Table 2). As suggested by Canfield (1998), therefore, it's likely that production of sulfate mainly provided a route, *via* sulfate-reducing bacteria, to delivery of excess sulfide to deep ocean waters and the consequent cessation of deposition of banded iron formations.

1800 Ma - present. Carbon-isotopic records from the Neoproterozoic onward are good enough that values of f can be estimated with some confidence (Hayes *et al.*, 1999). The results are crudely summarized in Figure 9a. When these values of f are applied to the carbon fluxes estimated here, the projected final total release of oxidizing power is 1920 Emol O_2 equiv. This is close to the average estimate of the total release represented by the sum of crustal Fe^{3+}, SO_4^{2-}, and O_2.

The agreement is notable, but discrepancies within the redox accounts are more impressive. Estimates of crustal inventories of oxidants vary by a factor of 1.7. Similarly, the estimated crustal inventories of organic carbon fall short (perhaps by 2×) of the summed inventories of oxidized products and of the estimated total burial of organic carbon (Fig. 9b). At face value, this requires that reduced products have been exported from the crust more efficiently than oxidized products. Unless organic carbon could be exported to the mantle more efficiently than Fe^{3+}, we are practically required to attribute such an imbalance to loss of H_2 from the top of the atmosphere. The redox imbalance and the likely importance of H_2 loss have been incisively examined and elaborated by Catling *et al.*(2001) and by Catling and Claire (2005). They associate loss of H_2 mainly with atmospheric CH_4 and thus with the Archean. By contrast, Tian et al. (2005) have noted the possible importance of the low exobase temperature of an anoxic atmosphere in limiting the rate of H_2 escape from the early earth. They contend that higher levels of O_2 in the atmosphere after 2.4 Ga would have increased exobase temperatures and promoted escape of hydrogen. Resolution of the history of hydrogen escape will constrain the second integral on the right side of eq. 10, and be a key step in reconstructing the time course of A_{Ox}.

The dearth of reduced products becomes particularly notable when the likely integrated effects of subduction, represented by the third integral in eq. 10, are considered. Lécuyer & Rickard (1999) contend that the *net* rate at which subduction is transferring Fe^{3+} from the crust to the mantle is presently 7 Tmol/yr, or 1.8 Tmol O_2 equiv/yr. If the continents are at steady state with respect to organic carbon, so that, in eq. 12, $f\gamma M + \gamma M_o = 0$, the rate at which the carbon cycle is releasing oxidizing power is given by (*cf.* eq. 12):

$$f[J_{am} - (J_{ad} + J_{od})] = 0.24(2.2 - 1.2) = 0.2 \text{ Tmol } O_2 \text{ equiv./yr} \qquad (13)$$

where the values substituted are center points of the ranges estimated in earlier sections of this paper. Since the net rate of subduction of Fe^{3+} proposed by Lécuyer & Rickard (1999) greatly exceeds this value, it is either incorrect or represents a temporary situation. Attention to subduction of Fe^{3+} is, however, a very good idea. The continuing release of oxidizing power, coupled with the minimal variations in atmospheric levels of O_2 during the Phanerozoic (Berner, 2004) and balanced exchange of oxidizing power by the cycles of carbon and sulfur during the same interval (Canfield, 2004), requires a continuing sink. It seems inescapable that this is supplied by oxidation of Fe^{2+} at the seafloor.

Bounds can be placed on the extent of this transfer over earth history, since iron returning to the mantle with a higher $Fe^{3+}/\Sigma Fe$ than it emerged with will result in oxidation of the upper mantle. There is a growing consensus that the redox state of the upper mantle, as measured by its oxygen fugacity, has not changed greatly over earth history. The recent constraint of Li & Lee (2004), from the V/Sc systematics of MOR basalts, indicates that the oxygen fugacity of the mantle source has increased by at most 0.3 log unit since 3.5 billion years ago. Using the relation of Kress & Carmichael (1991), this translates into a maximal 6% increase in the ferric iron content of the mantle, if all of that increase were attributable to addition of Fe^{3+}. Taking the mass of the upper mantle to be 1.34×10^{27} g (Ballentine et al. 2001), the mantle Fe content to be 6.3 wt% (Palme & O'Neill, 2003) and the mantle $Fe^{3+}/\Sigma Fe$ to be 0.12 (Bezos & Humler 2005), this yields a maximal input of 1.1×10^{22} mol of ferric iron since 3.5 Ga, or a maximum average input rate of 3 Tmol Fe^{3+}/yr (0.75 Tmol O_2 equiv.). This is comfortably within potential loads imposed by A_{Ox}.

The agreement between the projected release of oxidizing power and the average estimate of oxidized products is far from comforting. Because considerable amounts of Fe^{3+} must have been exported to the mantle, the total release of oxidizing power by the carbon cycle should exceed considerably the inventory of Fe^{3+} remaining in the crust. Part of any shortfall can be accommodated by recalling that the present estimates are minima. Finite values of J_{od} and a failure to reoxidize organic carbon in J_{or} will increase A_{Ox}.

The reburial of organic carbon can be treated quantitatively. If a portion, x, of J_{or} is simply reburied, two things will happen: (1) since it doesn't reenter the exogenic system as CO_2, that C will be unavailable for reduction. The organic burial flux and thus the overall production of oxidizing power will be decreased by an amount fxJ_{or}. (2) The oxidizing power consumed by oxidation of J_{or} will be reduced by an amount xJ_{or}. The first term is a loss of oxidizing power, the second is a gain. The difference is $(1 - f)xJ_{or}$. Unfortunately, this term cannot simply be added to eq. 12. Although it would account for the carbon and redox balances in a single increment of time, the proper treatment of subsequent increments would require that the reburied material be followed, with appropriate adjustments being made to sedimentary and continental inventories. Even during the Phanerozoic, the presence of detrital coal and kerogen in marine sediments (Sackett *et al.*, 1974) shows that x is not zero. On the other hand, it's known that microorganisms in weathering profiles incorporate carbon even from refractory kerogens (Petsch *et al.*, 2001) and that the great bulk of organic carbon in marine sediments is *not* recycled, detrital organic material. Under anaerobic conditions, however, reburial of organic carbon is likely to have been more important.

Can the carbon cycle operate at a point of redox neutrality, neither releasing nor consuming oxidants, even when isotopic compositions indicate significant rates of burial of organic carbon? The answer is in eq. 13. Even if burial and recycling are balanced, redox neutrality still requires $J_{am} = J_{ad} + J_{od}$. In other words, inputs from the mantle = outputs to the mantle. This is not a likely coincidence. Carbon flows into subduction zones not just from J_{am} but from multiple sources. If the portion of $J_{as} + J_{os} + J_{az}$ equal to J_{am} is to be returned to the mantle while the balance flows to J_{av} and J_{ov}, a very clever demon will be required to operate the carbon valve in the subduction zone. Notably, f (and thus $\delta_{ab} - \delta_{i}$) is not a measure of $J_{am} - (J_{ad} + J_{od})$. No particular value of δ_{ab} can be recognized as indicating redox neutrality. This yields two fundamental insights. First, caution is required when interpreting the isotopic record in terms of redox variations. Second, the conditions required for redox neutrality are precise and improbable.

Concluding Remarks

We have taken new approach to mass and redox balances involving the C cycle. Its principal strength is a realistic acknowledgement of the importance of inputs from and outputs to the mantle. This broader context has invited consideration of processes that may otherwise be overlooked or misconstrued. Its weakness is that our knowledge of some of the key processes is presently imprecise. We need to learn more about inputs of carbon, hydrogen escape, and processes in subduction zones to better evaluate each component of A_{Ox}. Even now, however, the resulting uncertainties do not cripple the approach. The key finding is dramatic: the persistence of δ_{ab} at values near zero rather than -5‰ can be interpreted only in terms of continuous and substantial releases of oxidizing power by the carbon cycle. Two points follow.

The oxidation of the crust has been more continuous than episodic. Increases in steady-state levels of oxidants derive either from combinations of geological and biological changes or from biological changes alone. The scientific problem of reconstructing earth's oxidation is more biological than geochemical.

Continuous sinks for oxidizing power are required, at least since atmospheric levels of O_2 stabilized at current levels approximately 550 Ma ago. Since exchanges of oxidizing power between the carbon and sulfur cycles have been balanced during that same time interval, this can have been provided only by the oxidation of iron.

Together, these affect our view of the carbon cycle. It should not be seen as the competent and versatile manager of an electron-transfer market, effortlessly balancing offers and bids. Instead, it's a wrong-way passenger on a down-going escalator. It continuously receives new CO_2 from the mantle, relentless supplies of solar energy, and nutrients leached from deposits that have retained their organic carbon. To hold its place, it must constantly produce new organic matter. While doing so, it releases oxidants that threaten to reverse its accomplishments. The stability of δ_{ab} is an indicator of the success of its evolutionary strategies. The stability of P_{O2} is evidence of an equally competent sink.

Acknowledgements

The seeds from which the ideas discussed have grown were planted when JMH looked out *Alvin*'s viewports and observed the H_2-rich waters of the Lost City hydrothermal vent system. The generosity of Deborah Kelley and Jeffrey Karson, the co-chief scientists of the Lost City cruise, is greatly appreciated. Since then, we have benefited from helpful and stimulating exchanges with Stan Hart, Don Anderson, David Rowley and Alberto Saal. We are very grateful for critical reviews of this manuscript provided by David Catling and Jennifer Eigenbrode. JMH receives support as a member of the Astrobiology team led by S. D'Hondt, University of Rhode Island. JRW is supported by an NDSEG Graduate Fellowship from the Office of Naval Research.

References

Aharon, Paul 2005 Redox stratification and anoxia of the early Precambrian oceans: Implications for carbon isotope excursions and oxidation events. *Precambrian Research* **137**, 207-222.

Alt, J. C. & Teagle, D. A. H. 1999 The uptake of carbon during alteration of ocean crust. *Geochimica et Cosmochimica Acta* **63**, 1527-1535.

Alt, J. C. & Teagle, D. A. H. 2003 Hydrothermal alteration of upper oceanic crust formed at a fast-spreading ridge: mineral, chemical, and isotopic evidence from ODP Site 801. *Chemical Geology* **201**, 191-211.

Arvidson, R. S., Mackenzie, F. T. & Guidry, M. 2005 MAGic: A Phanerozoic model for the geochemical cycling of major rock-forming components. *American Journal of Science* **in press**.

Bach, W., Peucker-Ehrenbrink, B, Hart, S. R. & Blusztajn, J. S. 2003 Geochemistry of hydrothermally altered oceanic crust: DSDP/ODP Hole 504B - Implications for seawater-crust exchange budgets and Sr- and Pb-isotopic evolution of the mantle. *Geochemistry, Geophysics, Geosystems G3* **4**, 1-29.

Ballentine, C. J., van Keken, P. E., Porcelli, D. & Houri, E. H. 2002 Numerical models, geochemistry and the zero-paradox noble-gas mantle. *Phil. Trans. R. Soc. Lond. A* **360**, 2611-2631.

Bekker, A., Karhu, J. A., Eriksson, K. A. & Kaufman, A. J. 2003 Chemostratigraphy of Paleoproterozoic carbonate successions of the Wyoming Craton: tectonic forcing of biogeochemical change? *Precambrian Research* **120**, 279-325.

Bekker, A., Holland, H. D., Wang, P. –L., Rumble, D. III, Stein, H. J., Hannah, J. L., Coetzee, L. L. And Beukes, N. J. 2004 Dating the rise of atmospheric oxygen. *Nature* **427**, 117-120.

Berner, R. A. 1991 A model for atmospheric CO_2 over Phanerozoic time. *American Journal of Science* **291**, 339-376.

Berner, R. A. & Maasch, K. A. 1996 Chemical weathering and controls on atmospheric O_2 and CO_2: Fundamental principles were enunciated by J. J. Ebelmen in 1845. *Geochimica et Cosmochimica Acta* **60**, 1633-1637.

Berner, R. A. 2004 *The Phanerozoic Carbon Cycle*. New York, NY, Oxford University Press.

Bezos, A. & Humler, E. 2005 The $Fe^{3+}/\Sigma Fe$ ratios of MORB glasses and their implications for mantle melting. *Geochimica et Cosmochimica Acta* **69**, 711-725.

Bjerrum, C. J. & Canfield, D. E. 2004 New insights into the burial history of organic carbon on the early Earth. *Geochemistry, Geophysics, Geosystems G3* **5**, 1-9.

Bjørnerud, M. G. & Austrheim, H. 2004 Inhibited eclogite formation: The key to the rapid growth of strong and Buoyant Archean continental crust. *Geological Society of America* **32**, 765-768.

Brocks, J. J., Buick, R., Logan, G. A. & Summons, R. E. 2003 Composition and syngeneity of molecular fossils from the 2.78 to 2.45 billion-year-old Mount Bruce Supergroup, Pilbara Craton, Western Australia. *Geochimica et Cosmochimica Acta* **67**, 4289-4319.

Broecker, W. S. 1970 A Boundary Condition on the Evolution of Atmospheric Oxygen. *Journal of Geophysical Research* **75**, 3553-3557.

Buick, I. S., Uken, R., Gibson, R. L. & Wallmach, T. 1998 High δ^{13}C Paleoproterozoic carbonates from the Transvaal Supergroup, South Africa. *Geology* **26**, 875-878.

Canfield, D. E. 1998 A new model for Proterozoic ocean chemistry. *Nature* **396,** 450-453.

Canfield, D. E. 2004 The evolution of the earth surface sulfur reservoir. *American Journal of Science*. **304**, 839-861.

Canfield, D. E. 2005 The early history of atmospheric oxygen: Homage to Robert A. Berner. *Ann. Rev. Earth & Planet. Sci.* **33**, 1-36.

Carmichael, I. S. E. 2002 The "andesite aqueduct" perspectives on the evolution of intermediate magmatism in west-central (105-99°W) Mexico. *Contributions to Mineralogy and Petrology* **143**, 641-663.

Catling, D. C. & Claire, M. W. 2005 How Earth's atmosphere evolved to an oxic state: A status report. *Earth Planet. Sci. Lett.* **237**, 1-20.

Catling, D. C., Zahnle, K. J. & McKay, C. P. 2001 Biogenic methane, hydrogen escape, and the irreversible oxidation of the early earth. *Science* **293**, 839-843.

Crisp, J. A. 1984 Rates of magma emplacement and volcanic output. *Journal of Volcanology and Geothermal Research* **20**, 177-211.

Dasgupta, R., Hirschmann, M., & Withers, A. C. 2004 Deep global cycling of carbon constrained by the solidus of anhydrous, carbonated eclogite under upper mantle conditions. *Earth and Planetary Science Letters* **227**, 73-85.

Deines, P., Viljoen, F. & Harris, J. W. 2001 Implications of the carbon isotope and mineral inclusion record for the formation of diamonds in the mantle underlying a mobile belt: Venetia, South Africa. *Geochimica et Cosmochimica Acta* **65**, 813-838.

Derry, L. A., Kaufman, A. J. & Jacobsen, S. B. 1992 Sedimentary cycling and environmental change in the Late Proterozoic: Evidence from stable and radiogenic isotopes. *Geochimica et Cosmochimica Acta* **56,** 1317-1329.

Des Marais, D. J. 1985 Carbon exchange between the mantle and the crust, and its effect upon the atmosphere: today compared to Archean time. *The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present.* E. T. Sundquist, W. S. Broecker (eds), American Geophysical Union, Geophysical Monograph 32, 602-611.

Des Marais, D. J. 2001 Isotopic Evolution of the Biogeochemical Carbon Cycle During the Precambrian. *Reviews in Mineralogy & Geochemistry* **43**, 555-578.

Dix, G. R., , Thomson, M. L., Longstaffe, F. J. & McNutt, R. H. 1995 Systematic decrease of high delta13C values with burial in late Archaean (2.8 Ga) diagenetic dolomite: evidence for methanogenesis from the Crixas Greenstone Belt, Brazil. *Precambrian Research* **70**, 253-268.

Eigenbrode, J. 2004 Late Archean Microbial Ecology: An Integration of Molecular, Isotopic, and Lithologic Studies. Ph.D. thesis, Earth Sciences, the Pennsylvania State University.

Farquhar, J. & Wing, B. A. 2003 Multiple sulfur isotopes and the evolution of the atmosphere. *Earth and Planetary Science Letters* **213**, 1-13.

Garrels, R. M. & Perry, E. A. Jr. 1974 Cycling of carbon, sulfur, and oxygen through geologic time. *The Sea* **5**, 303-336.

Garrels, R. M. & Lerman, A. 1981 Phanerozoic cycles of sedimentary carbon and sulfur. *Geology* **78**, 4652-4655.

Giggenbach, W. F. 1996 Chemical Composition of Volcanic Gases. *Monitoring and Mitigation of Volcano Hazards*, S. Scarpa and R. I. Tilling, eds. Berlin, Springer Verlag, 221-256.

Halmer, M. M., Schmincke, H.-U. & Graf, H.-F. 2002 The annual volcanic gas input into the atmosphere, in particular into the stratosphere: a global data set for the past 100 years. *J. Volcanol. Geothermal Res.* **115**, 511-528.

Halverson, G. P., Hoffman, P. F., Schrag, D. P., Maloof, A. C. & Rice, A. H. H. 2005 Toward a Neoproterozoic composite carbon-isotope record. *Geological Society of America* **117**, 1181-1207.

Hayes, J. M. 1983 Geochemical evidence bearing on the origin of aerobiosis, a speculative interpretation. *The Earth's earliest biosphere: its origin and evolution*. J. W. Schopf, Princeton University Press, 291-301.

Hayes, J. M. 1994 Global methanotrophy at the Archean-Proterozoic transition. *Early Life on Earth. Nobel Symposium.* S. Bengtson, Columbia University Press, New York. **84**, 220-236.

Hayes, J. M., Kaplan, I. R. & Wedeking, K. W. 1983 Precambrian organic geochemistry, preservation of the record. *The Earth`s earliest biosphere: its origin and evolution*. J. W. Schopf, Princeton University Press, 93-134.

Hayes, J. M., Lambert, I. B. & Strauss, H. 1992 The sulfur-isotopic record. *The Proterozoic Biosphere, a Multidisciplinary Study*. J. W. Schopf and C. Klein, Cambridge University Press, 129-132.

Hayes, J. M., Strauss, H. & Kaufman, A. J. 1999 The abundance of ^{13}C in marine organic matter and isotopic fractionation in the global biogeochemical cycle of carbon during the past 800 Ma. *Chemical Geology* **161**, 103-125.

Hilton, D. R., Fischer, T. & Marty, B. 2002 Noble Gases and Volatile Recycling at Subduction Zones. *MSA Special Volume: Noble Gasses* **47**, 319-370.

Hofmann, A. W. 2004 Sampling Mantle Heterogeneity through Oceanic Basalts: Isotopes and Trace Elements. *Treatise on Geochemistry*. H. D. Holland, K. K. Turekian (eds), Elsevier Ltd, Oxford. Vol. 2, 61-101.

Holland, H. D. 1978 *The Chemistry of the Atmosphere and Oceans.* J. Wiley & Sons, New York.

Holland, H. D. 1984 *The Chemical Evolution of the Atmosphere and Oceans*. Princeton, NJ, Princeton University Press.

Holland, H. D. 2002 Volcanic gases, black smokers, and the Great Oxidation Event. *Geochimica et Cosmochimica Acta* **66**; 3811-3826.

Holser, W. T., Schidlowski, M., MacKenzie, F. T. & Maynard, J. B. 1988 *Geochemical Cycles of Carbon and Sulfur. Chemical Cycles in the Evolution of the Earth*. C. B. Gregor, R. M. Garrels, F. T. Mackenzie and J. B. Maynard. New York, NY, John Wiley & Sons: 105-173.

Hunt, J. M. 1996 *Petroleum Geochemistry and Geology*. New York, NY, W. H. Freeman & Company.

Ingebritsen, S. E. & Manning, C. E. 2002 Diffuse fluid flux through orogenic belts: Implications for the world ocean. *Proc. Nat. Acad. Sci. U. S. A.* **99**, 9113-9116.

Irwin, H., Curtis, C. D. & Coleman, M. L. 1977 Isotopic evidence for source of diagenetic carbonates formed during burial of organic rich sediments. *Nature* **269**, 209-213.

Jiao, Y., Kappler, A., Croal, L. R., & Newman, Dianne K. 2005 Isolation and Characterization of a Genetically Tractable Photoautotrophic Fe(II)-Oxidizing Bacterium, Rhodopseudomonas palustris Strain TIE-1. *Applied and Environmental Microbiology* **71,** 4487-4496.

Kadko, D. 1994 An assessment of the effect of chemical scavenging within hydrothermal plumes upon ocean geochemistry. *Earth Planet. Sci. Lett.* **120** 361-374.

Karhu, J. A. & Holland, H. D. 1996 Carbon isotopes and the rise of atmospheric oxygen. *Geology* **24**, 867-870.

Kasting, J. F. & Catling, D. 2003 Evolution of a Habitable Planet. Annu. Rev. Astron. *Astrophys*. **41**, 429-463.

Kerrick, D. M. & Connolly, J. A. D. 2001 Metamorphic devolatilization of subducted oceanic metabasalts: implications for seismicity, arc magmatism and volatile recycling. *Earth and Planetary Science Letters* **189**, 19-29.

Klein, J. S., Mozley, P., Campbell, A. & Cole, R. 1999 Spatial distribution of carbon and oxygen isotopes in laterally extensive carbonate-cemented layers: implications for mode of growth and subsurface identification. *Journal of Sedimentary Research* **69**, 184-191.

Knoll, A. H., Hayes, J. M., Kaufman, A. J., Swett, K. & Lambert, I. B. 1986 Secular variation in carbon isotope ratios from Upper Proterozoic successions of Svalbard and East Greenland. *Nature* **321**, 832-838.

Kopp, R. E., Kirschvink, J. L., Hilburn, I. A. & Nash, C. Z. 2005 The Paleoproterozoic snowball Earth: A climate disaster triggered by the evolution of oxygenic photosynthesis. *PNAS* **102** 11131-11136.

Kress, V. C. & Carmichael, I. S. E. 1991 The compressibility of silicate liquids containing Fe203 and the effect of composition, temperature, oxygen fugacity and pressure on their redox states. *Contributions to Mineralogy and Petrology* **108**, 82-92.

Kump, L. R. & Arthur, M. A. 1999 Interpreting carbon-isotope excursions: carbonates and organic matter. *Chemical Geology* **161**, 181-198.

Kyser, T. K. 1986 Stable Isotope Variations in the Mantle. Stable Isotopes in High Temperature Geological Processes. *Reviews in Mineralogy* **16**, 141-164.

Lécuyer, C. & Ricard, Y. 1999 Long-term fluxes and budget of ferric iron: implication for the redox states of the Earth's mantle and atmosphere. *Earth and Planetary Science Letters* **165**, 197-211.

Li, Z.-X. A. & Lee, C-T. A. 2004 The constancy of upper mantle fO2 through time inferred from V/Sc ratios in basalts. *Earth and Planetary Science Letters* **228**, 483-493.

Lowe, D. R. 1992 Major events in the geological development of the Precambrian Earth. *The Proterozoic Biosphere*. Schopf , J. W., Klein, C. (eds), Cambridge University Press: 67-76.

Lowell, R. P. & Keller, S. M. 2003 High-temperature seafloor hydrothermal circulation over geologic time and Archean banded iron formations. *Geophysical Research Letters* **30**, 1-44.

Luth, R. W. 2004 Mantle Volatiles—Distribution and Consequences. *Treatise on Geochemistry*. H. D. Holland, K. K. Turekian (eds), Elsevier Ltd, Oxford. Vol. 2, need pages.

Marty, B. & Tolstikhin, I. N. 1998 CO_2 fluxes from mid-ocean ridges, arcs and plumes. *Chemical Geology* **145**, 233-248.

Mattey, D. P. 1987 Carbon isotopes in the mantle. *Terra Cognita* **7**, 31-37.

Mazzullo, S. J. 2000 Organogenic dolomitization in peritidal to deep-sea sediments. *Journal of Sedimentary Research* **70**, 10-23

Melezhik, V. A. Fallick, A. E., Medvedev, P. V. & Makarikhin, V. V. 1999 Extreme $^{13}C_{carb}$ enrichment in ca. 2.0 Ga magnesite-stromatolite--dolomite--"red beds" association in a global context: a case for the world-wide signal enhanced by a local environment. *Earth-Science Reviews* **48**, 71-120.

Milkov, A. V. & Etiope, G. 2005 Global methane emission through mud volcanoes and its past and present impact on the Earth's climate--a comment. *Int J Earth Sci (Geol Rundsch*) **94**, 490-492.

Milkov, A. V. 2005 Molecular and stable isotope compositions of natural gas hydrates: A revised global dataset and basic interpretations in the context of geological settings. *Organic Geochemistry* **36**, 681-702.

Nakamura, K. & Kato, Y. 2004 Carbonatization of oceanic crust by the seafloor hydrothermal activity and its significance as a CO2 sink in the Early Archean. *Geochimica et Cosmochimica Acta* **68**, 4595-4618.

Palme, H. & O'Neill, H. S. C. 2003 Cosmochemical Estimates of Mantle Composition. *Treatise on Geochemistry*. H. D. Holland, K. K. Turekian (eds), Elsevier Ltd, Oxford. Vol. 2, 1-38.

Pavlov, A. A. & Kasting, J. F. 2002 Mass-independent fractionation of sulfur isotopes in Archean sediments: strong evidence for an anoxic Archean atmosphere. *Astrobiology* **2**, 27-41.

Pearson, D. G., Canil, D. & Shirey, S. B. 2004 Mantle Samples Included in Volcanic Rocks: Xenoliths and Diamonds. *Treatise on Geochemistry*. H. D. Holland, K. K. Turekian (eds), Elsevier Ltd, Oxford. Vol. 2, 172-221.

Petsch, S. T., Eglinton, T. I. & Edwards, K. J. 2001 ^{14}C-Dead Living Biomass: Evidence for Microbial Assimilation of Ancient Organic Carbon During Shale Weathering. *Science* **292**, 1127-1131.

Pineau, F., Cartigny, P. & Javoy, M. 2004 Carbon flux and C/Nb ratios in the mantle in ridge context, *Eos Trans. AGU* **85**, Fall Meet. Suppl., Abstract V31C-1453P.

Plank, T. & Langmuir, C. H. 1998 The chemical composition of subducting sediment and its consequences for the crust and mantle. *Chemical Geology* **145,** 325-394.

Quay, P., Sonnerup, P., Westby, T., Stutsman, J. & McNichol, A. 2003 Changes in the $^{13}C/^{12}C$ of dissolved inorganic carbon in the ocean as a tracer of anthropogenic CO_2 uptake. *Global Biogeochemical Cycles* **17**, 1-4.

Resing, J. A., Lupton, J. E., Feely, R. A. & Lilley, M. D. 2004 CO_2 and ^3He in hydrothermal plumes: implications for mid-ocean ridge CO_2 flux. *Earth and Planetary Science Letters* **226,** 449-464.

Rothman, D. H., Hayes, J. M. & Summons, R. E. 2003 Dynamics of the Neoproterozoic carbon cycle. *Proceedings of the National Academy of Sciences USA* **100**, 8124-8129.

Rowley, D. B. 2002 Rate of plate creation and destruction: 180 Ma to present. *Geological Society of America Bulletin* **114**, 927-933.

Saal, A. E., Hauri, E. H., Langmuir, C. H., & Perfit, M. R. 2002 Vapour undersaturation in primitive mid-ocean-ridge basalt and the volatile content of Earth's upper mantle. *Nature* **419,** 451-446.

Sackett, W. M., Poag, C. W., & Eadie, B. J. 1974 Kerogen Recycling in the Ross Sea, Antarctica. *Science* **185,** 1045-1047.

Sano, Y. & Marty, B. 1995 Origin of carbon in fumarolic gas from island arcs. *Chemical Geology* **119,** 265-274.

Sano, Y. & Williams, S. N. 1996 Fluxes of mantle and subducted carbon along convergent plate boundaries. *Geophysical Research Letters* **23**, 2749-2752.

Schidlowski, M., Eichmann, R. & Junge, C. E. 1975 Precambrian sedimentary carbonates: carbon and oxygen isotope geochemistry and implications for the terrestrial oxygen budget. *Precambrian Research* **2**, 1-69.

Shackleton, N. J. 1987 The carbon isotope record of the Cenozoic: history of organic carbon burial and of oxygen in the ocean and atmosphere. Marine Petroleum Source Rocks. J. F. Brooks, A. J., *Geological Society Special Publication No***. 26**, 423-434.

Shaw, A. M., Hilton, D. R., Fischer, T. P., Walker, J. A., & Alvarado, G. E. 2003 Contrasting He-C relationships in Nicaragua and Costa Rica: insights into C cycling through subduction zones. *Earth and Planetary Science Letters* **214**, 499-513.

Shaw, A. M., Hilton, D. R., Macpherson, C. G. & Sinton, J. M. 2004 The CO2-He-Ar-H2O systematics of the Manus back-arc basin: Resolving source composition from degassing and contamination effects. *Geochimica et Cosmochimica Acta* **68**, 1837-1856.

Shields, G. & Veizer, J. 2002 Precambrian marine carbonate isotope database: Version 1.1. *Geochemistry, Geophysics, Geosystems G3* **3,** 1-12.

Sleep, N. H. & Zahnle, K. 2001 Carbon dioxide cycling and implications for climate. *Journal of Geophysical Research* **106**, 1373-1399.

Sleep, N. H., Meibom, A., Fridriksson, T., Coleman, R. G. & Bird, D. K. 2004 H_2-rich fluids from serpentinization: Geochemical and biotic implications. *PNAS* **101**, 12818-12823.

Staudigel, H., Hart, S. R., Schmincke, H.-u. & Smith, B. M. 1989 Cretaceous ocean crust at DSDP Sites 417 and 418: Carbon uptake from weathering versus loss by magmatic outgassing. *Geochimica et Cosmochimica Acta* **53**, 3091-3094.

Stern, R. J. 2005 Evidence from ophiolites, blueschists, and ultrahigh-pressure metamorphic terranes that the modern episode of subduction tectonics began in Neoproterozoic time. *Geological Society of America* **33**, 557-560.

Strauss, H. & Moore, T. B. 1992 Abundances and Isotopic Compositions of Carbon and Sulfur Species in Whole Rock and Kerogen Samples. *The Proterozoic Biosphere*. Schopf , J. W., Klein, C. (eds), Cambridge University Press: 709-798.

Su, Y., and Langmuir, C. H. 2003 Global MORB chemistry compilation at the segment scale. Database available at http://www.petdb.org.

Summons, R. E., Jahnke, L. L., Hope, J. M. & Logan, G. A. 1999 2-Methylhopanoids as biomarkers for cyanobacterial oxygenic photosynthesis. *Nature* **400**, 554-557.

Tajika, E. 2003 Faint young sun and the carbon cycle: implications for the Proterozoic global glaciations. *Earth Planet. Sci. Lett.* **214**, 443-453.

Tappert, R., T., Stachel, T., Harris, J. W. Muehlenbachs, K., Lugwig, T. & Grey, G. P. 2005 Subducting oceanic crust: The source of deep diamonds. *Geological Society of America Bulletin* **33**, 565-568.

Tian, F., Toon, O. B., Pavlov, A. A. & De Sterck, H. 2005 A Hydrogen-Rich Early Earth Atmosphere. *Science* **308**, 1014-1017.

Tice, M. M. and Lowe, D. R. 2004 Photosynthetic microbial mats in the 3,416-Myr-old ocean. *Nature* **431**, 549-552.

Van Kranendonk, M. 2004 Archean Tectonics 2004: A review. *Precambrian Research* **131**, 143-151.

Veizer, J., D., Davin, A., Azmy, K., Bruckschen, P., Buhl, D., Bruhn, F., Carden, G. A., Diener, A., Ebneth, S. Godderis, Y., Jasper, T., Korte, C., Powellek, F., Podluha, O. G. & Strauss, H. 1999 ^{87}Sr/^{86}Sr, and δ^{18}O evolution of Phanerozoic seawater. *Chemical Geology* **161**, 59-88.

Veizer, J. and Mackenzie, F. T. 2004 Evolution of Sedimentary Rocks. *Treatise on Geochemistry*. H. D. Holland, K. K. Turekian (eds), Elsevier Ltd, Oxford. Vol. **7,** 369-407.

Walker, J. C. G. 1987 Was the Archean biosphere upside down? *Nature* **329**, 710-712.

Walker, J. C. G. 1990 Precambrian evolution of the climate system. *Palaeogeography, Palaeoclimatology, Palaeoecology* **82**, 261-289.

Wallace, P. J. 2005 Volatiles in subduction zone magmas: concentrations and fluxes based on melt inclusion and volcanic gas data. *Journal of Volcanology and Geothermal Research* **140**, 217-240.

Wedepohl, K. H. 1995 The composition of the continental crust. *Geochim. Cosmochim. Acta* **59**, 1217-1232.

White, R. S., McKenzie, D. P., and O'Nions, R. K. 1992 Oceanic crustal thickness from seismic measurements and rare earth element inversions. *J. Geophys. Res.* **97** 683-714.

Wilkinson, B. H. and Walker, J. C. G. 1989 Phanerozoic cycling of sedimentary carbonate. *American Journal of Science* **289**, 525-548.

Young, G. M., Long, D. G. F., Fedo, C. M. and Nesbitt, H. W. 2001 Paleoproterozoic Huronian basin: product of a Wilson cycle punctuated by glaciations and a meteorite impact. *Sedimentary Geology* **141-142**, 233-254.

Yudovich, Y. E., Makarikhin, V. V., Medvedev, P. V. and Sukhanov, N. V. 1991 Carbon isotope anomalies in carbonates of the Karelian Complex. *Geochemistry International* 28, 56-62.

Figure Captions

Figure 1. A schematic representation of the biogeochemical cycle of carbon. The arrows represent fluxes of carbon that are explained in the text.

Figure 2. Graphs indicating relationships between *f* and δ_{ab} - δ_l (eq. 7). Slopes and intercepts vary in response to varying values of ε, λ, Δ_m, and Δ_g. In each frame, one of these has been assigned four different values and the others have been held constant. The values assigned are indicated in each frame. For the parameter that varies, the sequence of values corresponds to the lines as seen from left to right.

Figure 3. A schematic view of flows of oxidants and reductants generated by the carbon cycle. Sites of oxidation are marked by the letter O.

Figure 4. Estimated values of J_{am} as a function of time. The value at 0 Ma is documented in the text. The scaling relationship at earlier times derives from Sleep and Zahnle (2001) and Lowell and Keller (2003).

Figure 5. Total amount of mantle carbon delivered to the crust as a function of time. Specifically,

$$\text{Total Mantle-to-Crust C} = \sum_{3800}^{t} J_{\text{am}}(t) \cdot \tau$$

where *t* is the age, Ma, and τ, the time step, is 10^7 yr. The broken line at 8500 Emol C represents the best estimate of the present crustal inventory of C (Table 2).

Figure 6. Schematic view of fluxes of carbon and reducing power in a subduction zone. Terms denote $Fe^{3+}/\Sigma Fe$ (φ), and fluxes of carbon (*J*, moles/time), specific substances (*j*, moles/time) and oxidizing or reducing power (*L*, moles O_2 equivalent/time). Subscripts are defined in Table 1. Chemical reductions and oxidations are marked by circled letters (R or O). Adjacent numbers indicate number of electrons gained or lost.

Figure 7. Growth of the crustal inventory of carbon over time. (a) Outputs to the mantle relative to inputs from the mantle as a function of time. The ratio is assumed to be near unity when continents were nonexistent and to have declined as they increased in size. Values have be adjusted to provide the observed total of 8500 Emol C by 0 Ma. (b) The integral obtained by applying the return fraction specified in panel a, above, to the fluxes shown in Figure 4. In detail,

$$\text{Total Crustal C} = \sum_{3800}^{t} J_{\text{am}}(t) \cdot \left[1 - \frac{J_{\text{ad}}(t) + J_{\text{od}}(t)}{J_{\text{am}}(t)}\right] \cdot \tau$$

Figure 8. Isotopic compositions of sedimentary carbonates and of sedimentary organic carbon as a function of time. Each point represents the average isotopic composition of an entire stratigraphic unit. Carbonates (Shields & Veizer, 2002) are represented by circles. Filled symbols represent geologic units which are well dated. Open symbols represent units for which the dates are approximate. Samples of organic material (Strauss & Moore, 1992) are represented by triangles. The ages assigned in the original compilation have been revised to agree with those assigned by Shields and Veizer (2002).

Figure 9. Integrated net production of organic carbon, equivalent to the net release of oxidizing power (Emol O_2), over time. (a) Estimated values of *f*. For ages greater than 890 Ma, they are based on the isotopic compositions shown in Figure 8. For younger ages, they are consistent with the isotopic

compositions shown in Figure 8 and are based in detail on records summarized by Hayes *et al.* (1999). The broken lines between 2080 and 2400 Ma represent isotopic excursions reviewed by Melezhik *et al.* (1999) and discussed in the text. (b) The integral obtained when the f values shown in Figure 9a and the carbon-return ratios shown in Figure 7a are substituted in eq. 12, with $\gamma = 0.023$ and $M = M_o = 0$ at 3800 Ma.

Figure 10. Summary of a sequence of conditions that could account for the abundance of ^{13}C-enriched sedimentary carbonates 2400-2080 Ma ago.

Table 1. Definitions

Main Variables

Term	Definition
A_{Ox}	Rate of accumulation of oxidants in crust, (moles O_2 equivalent)/time
J	Flux of carbon, moles/time
L	Flux of oxidant or reductant, (moles O_2 equivalent)/time
M	Molar quantity of C (no subscript: total crustal carbon, all forms)
f	Fraction of C buried in organic form, $= J_{\mathrm{ob}}/(J_{\mathrm{ab}} + J_{\mathrm{aw}} + J_{\mathrm{ob}})$
j_{x}	Flux of substance x, moles/time
Δ_{g}	Isotopic difference between DIC in surface seawater and diagenetically stabilized carbonate minerals in sedimentary rocks, ‰. See eq. 4
Δ_{m}	Isotopic difference between DIC in surface seawater and carbonate in weathered oceanic basalts, ‰. See eq. 6
γ	Fraction of crustal C recycling during τ. $\gamma = (1 - e^{-k\tau})$ where k = (ln 2)/(half-mass age).
δ	$\delta^{13}C_{\mathrm{VPDB}}$, ‰
ε	Isotopic fractionation between DIC in surface seawater and sedimentary organic carbon, ‰. See eq. 5
φ	$Fe^{3+}/\Sigma Fe$
λ	Fraction of buried carbonate accounted for by ocean-crustal carbonates, $= J_{\mathrm{aw}}/(J_{\mathrm{aw}} + J_{\mathrm{ab}})$
τ	Step time in numerical integrations, 10^7 yr; Figures 5, 7, and 9

Subscripts appended to J, L, and δ

First or only part

Ox	Oxidant
Red	Reductant
a	Carbonate carbon
i	Input to exogenic reaction chamber. See eq. 3.
o	Organic carbon

Second part, pertaining to a directional flux

b	**b**urial, transfer from exogenic reaction chamber to deep sediments
c	transfer from deep sediments to continental crust
d	transfer from subduction zone to mantle
h	transfer from ocean crust to continental crust
m	transfer from mantle to exogenic reaction chamber
r	(**r**eturns) transfer from continent to exogenic reaction chamber
s	(**s**ubduction) transfer from deep sediments to subduction zone
v	(**v**olcanism) transfer from subduction zone to exogenic reaction chamber
w	(**w**eathering) transfer from exogenic reaction chamber to ocean crust
x	transfer from exogenic reaction chamber to space
z	transfer from ocean crust to subduction zone

Table 2. Crustal Inventories of Reduced and Oxidized Products of Carbon Cycling[a]

	Estimated Crustal Total Emol O_2 equivalent		
Product	High	Low	Reference
O_2	37.2	37.2	Keeling *et al.*, 1993
Fe^{3+} [b]	1860		Goldschmidt, 1954
		1020	Ronov & Yaroshevsky, 1976
SO_4^{2-}	480		Garrels & Perry, 1974
		332	Holser *et al.*, 1988
Total oxidants	2377	1389	
Organic C	1280		DesMarais, 2001
		675	Arvidson *et al.*, 2005

---

[a] A similar compilation has been prepared by Catling *et al.* (2001). It includes an estimate of 1000 Emol organic C delivered to the crust by impacts of asteroids between 4400 and 3800 Ma. The entries above pertain to the present. To whatever extent primordial organic material has survived in the crustal inventory, it is included in the "Organic C" category.

[b] Calculated from data summarized by Lécuyer & Rickard (1999). Represents Fe^{3+} in excess over mantle $Fe^{3+}/\Sigma Fe = 0.12$ (Bezos & Humler, 2005).

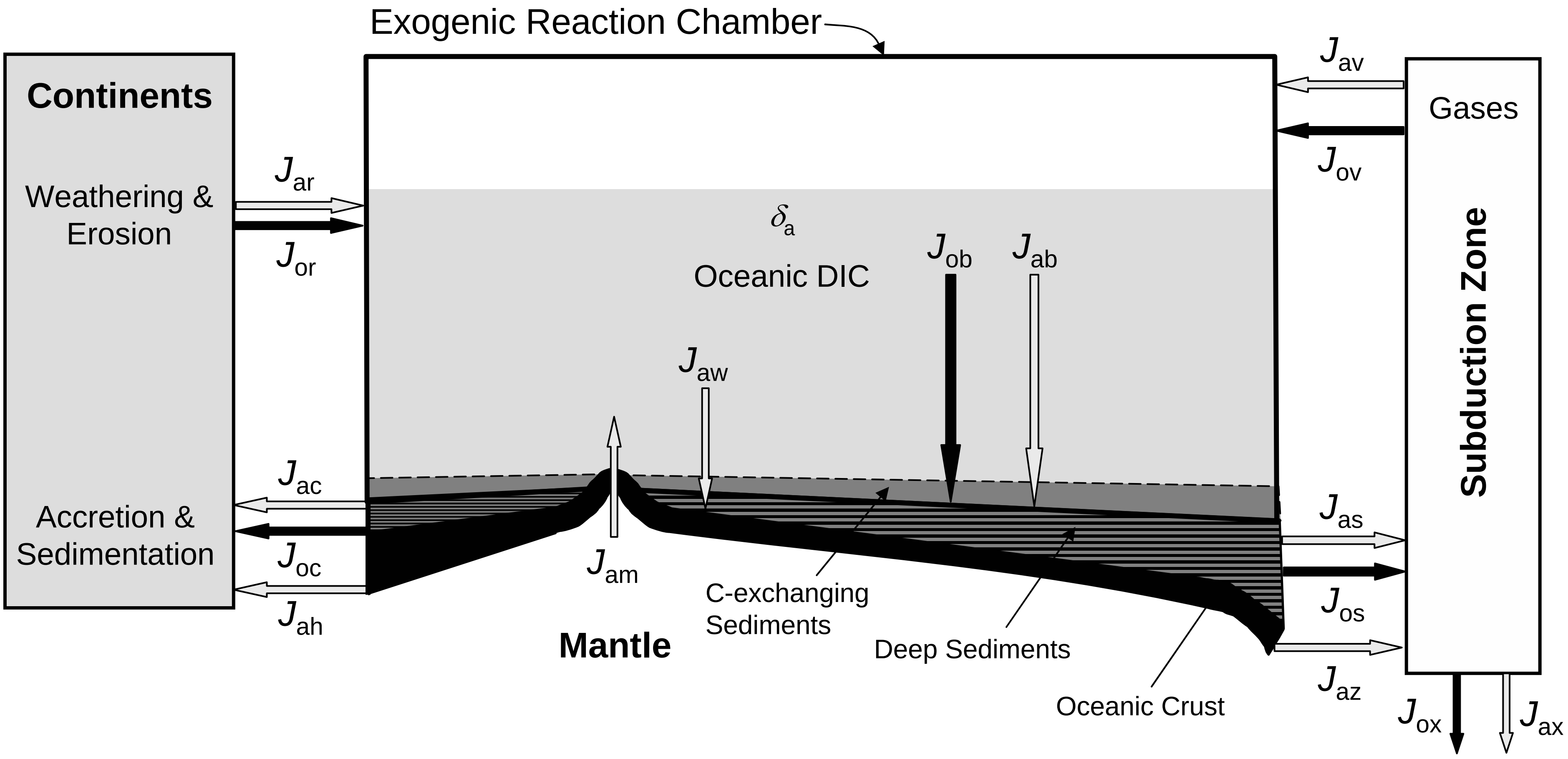
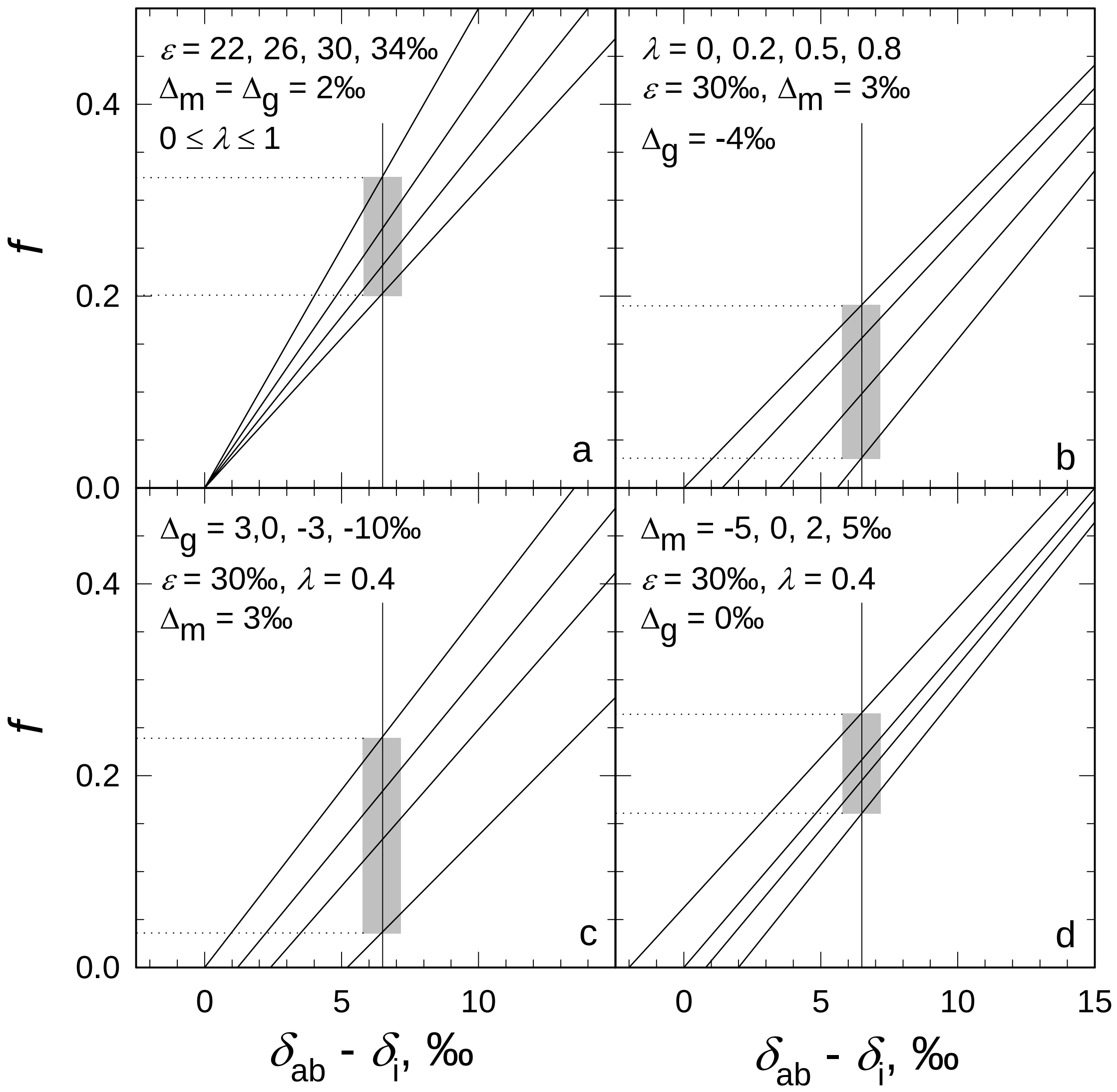

Exogenic Reaction Chamber
Continents
Weathering & Erosion
J_{ar}
J_{or}
Accretion & Sedimentation
J_{ac}
J_{oc}
J_{ah}
δ_a
Oceanic DIC
J_{ob}
J_{ab}
J_{aw}
J_{am}
Mantle
C-exchanging Sediments
Deep Sediments
Oceanic Crust
J_{av}
J_{ov}
Gases
Subduction Zone
J_{as}
J_{os}
J_{az}
J_{ox}
J_{ax}

Figure 1



ε = 22, 26, 30, 34‰
$\Delta_m = \Delta_g$ = 2‰
$0 \leq \lambda \leq 1$
a
λ = 0, 0.2, 0.5, 0.8
ε = 30‰, Δ_m = 3‰
Δ_g = -4‰
b
Δ_g = 3,0, -3, -10‰
ε = 30‰, λ = 0.4
Δ_m = 3‰
c
Δ_m = -5, 0, 2, 5‰
ε = 30‰, λ = 0.4
Δ_g = 0‰
d
f
0.0
0.2
0.4
0
5
10
15
$\delta_{ab} - \delta_i$, ‰

Figure 2

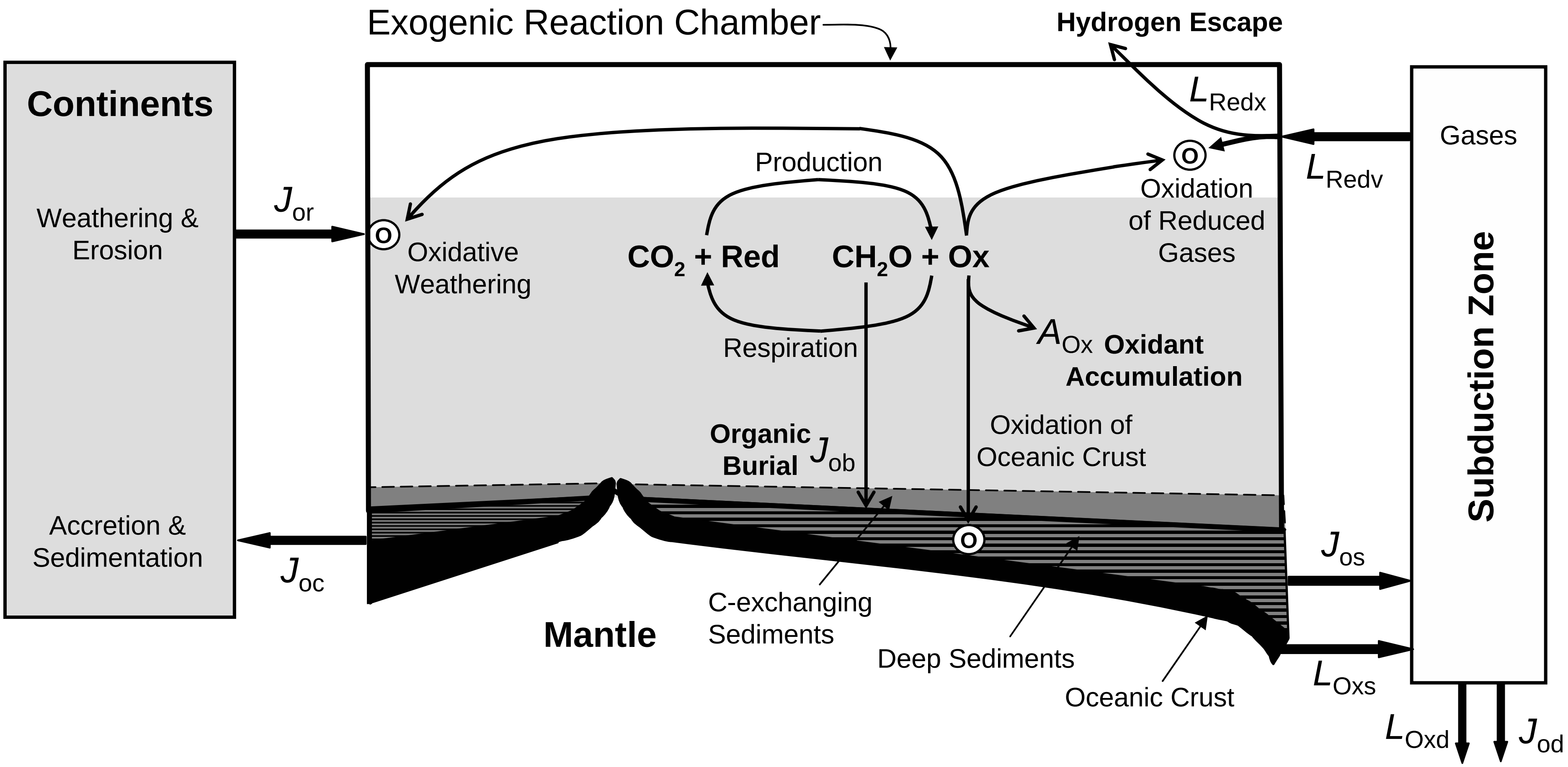
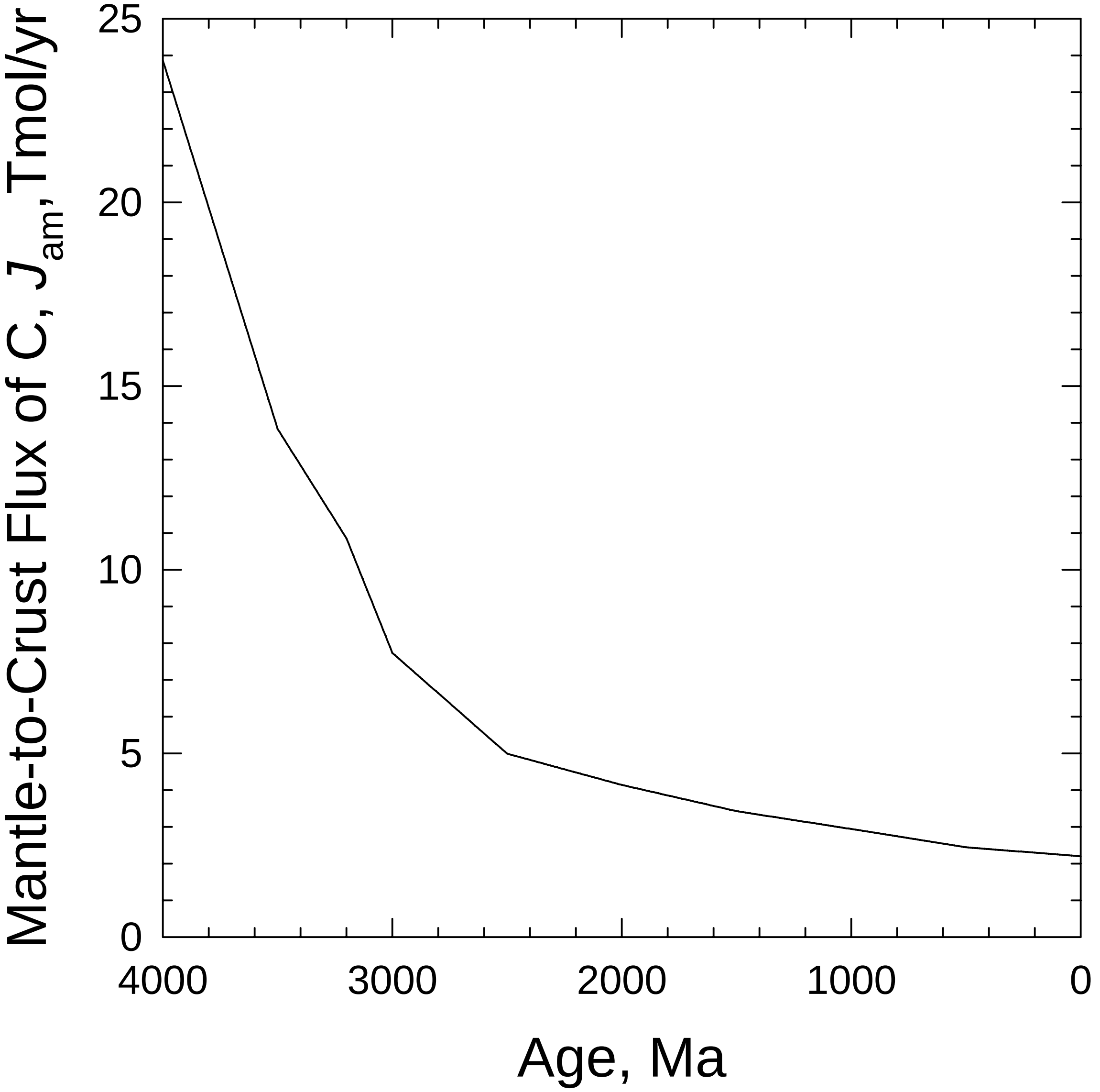

Exogenic Reaction Chamber
Hydrogen Escape
Continents
Weathering & Erosion
J_{or}
O
Oxidative Weathering
Production
CO_2 + Red
CH_2O + Ox
Respiration
L_{Redx}
O
Oxidation of Reduced Gases
Gases
L_{Redv}
Subduction Zone
A_{Ox} Oxidant Accumulation
Organic Burial J_{ob}
Oxidation of Oceanic Crust
Accretion & Sedimentation
J_{oc}
O
J_{os}
Mantle
C-exchanging Sediments
Deep Sediments
Oceanic Crust
L_{Oxs}
L_{Oxd}
J_{od}

Figure 3



Mantle-to-Crust Flux of C, J_{am}, Tmol/yr
25
20
15
10
5
0
4000
3000
2000
1000
0
Age, Ma

Figure 4

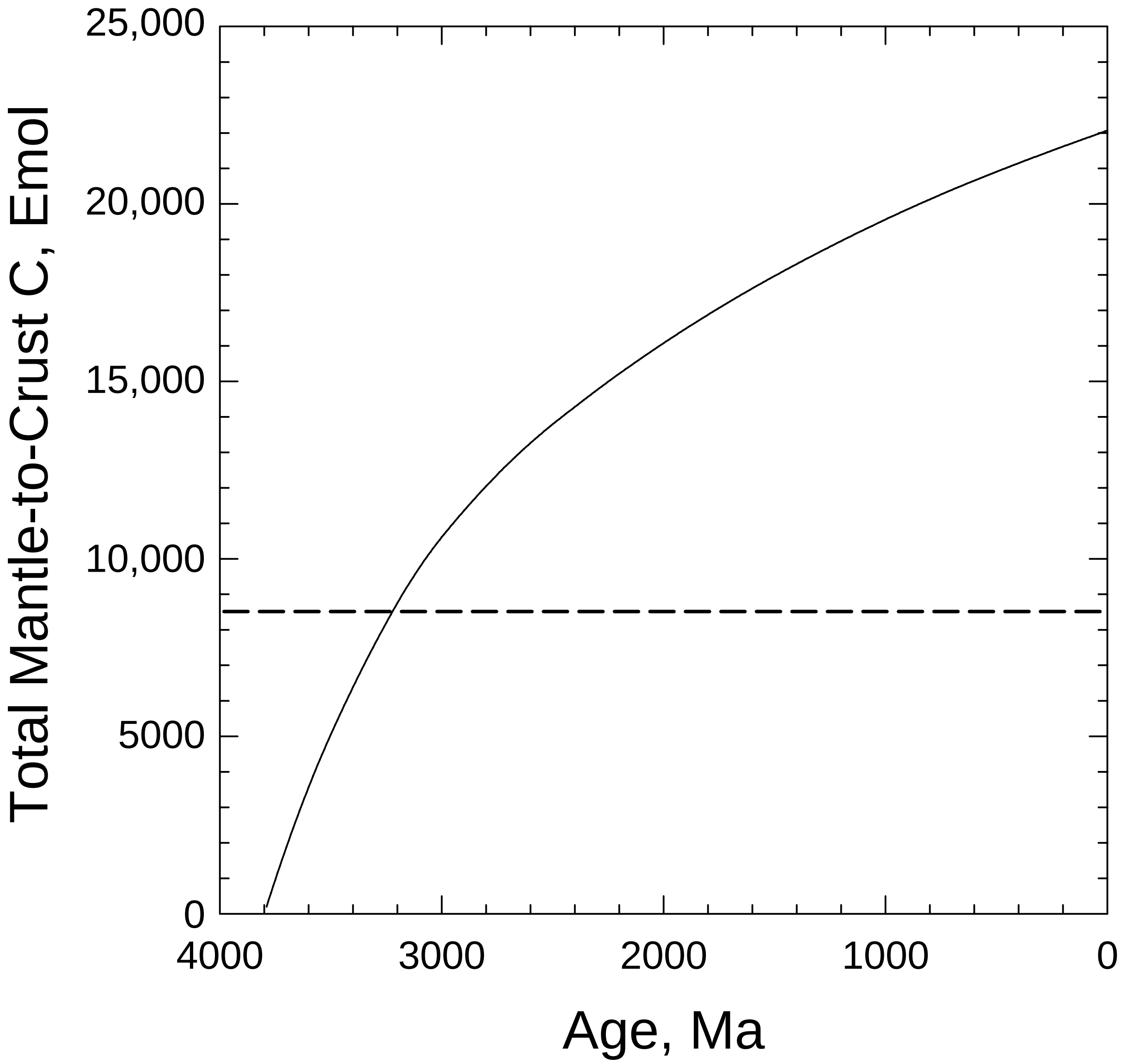
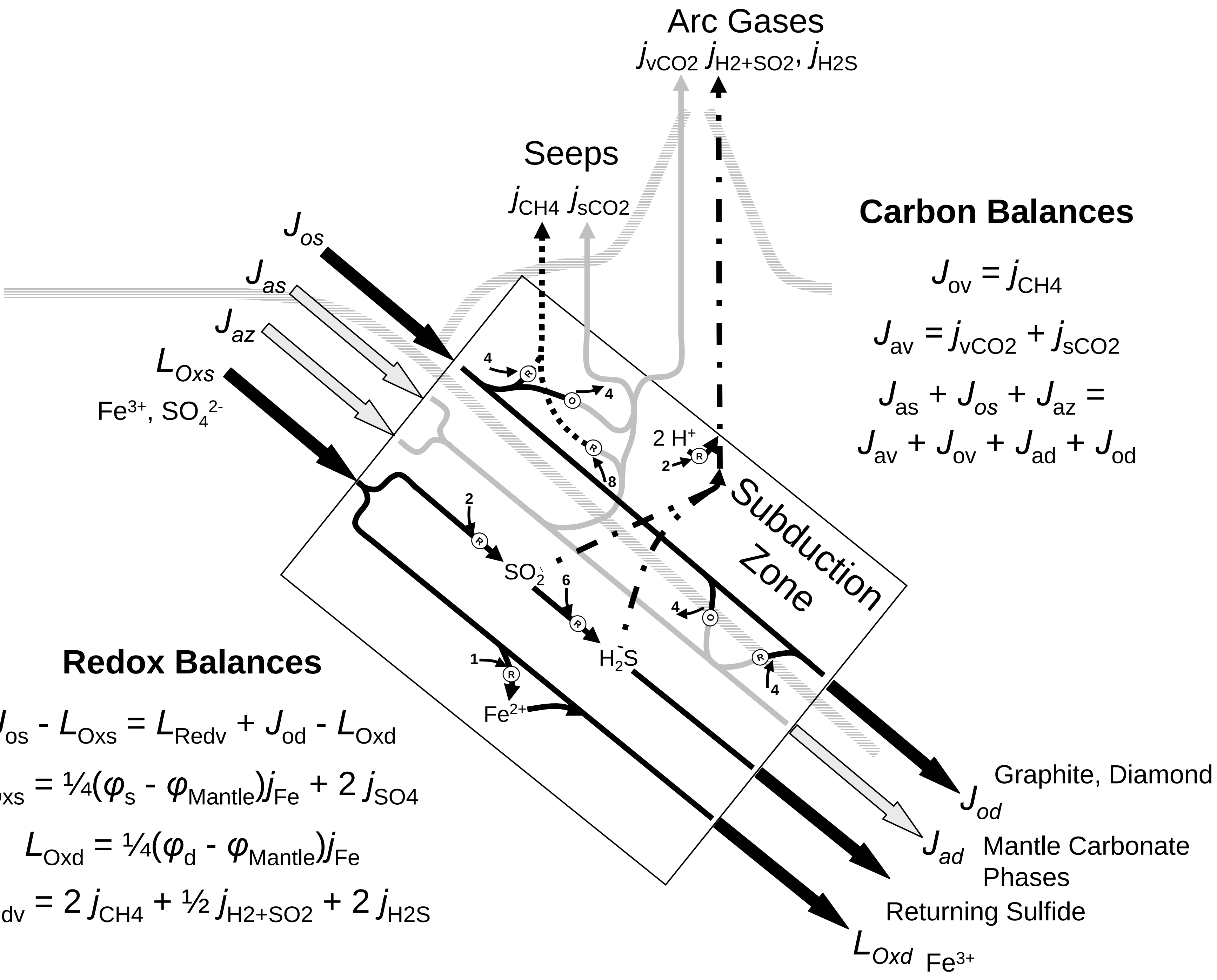

25,000
20,000
15,000
10,000
5000
0
Total Mantle-to-Crust C, Emol
4000
3000
2000
1000
0
Age, Ma

Figure 5



Carbon Balances

$$J_{ov} = j_{CH4}$$

$$J_{av} = j_{vCO2} + j_{sCO2}$$

$$J_{as} + J_{os} + J_{az} = J_{av} + J_{ov} + J_{ad} + J_{od}$$

Redox Balances

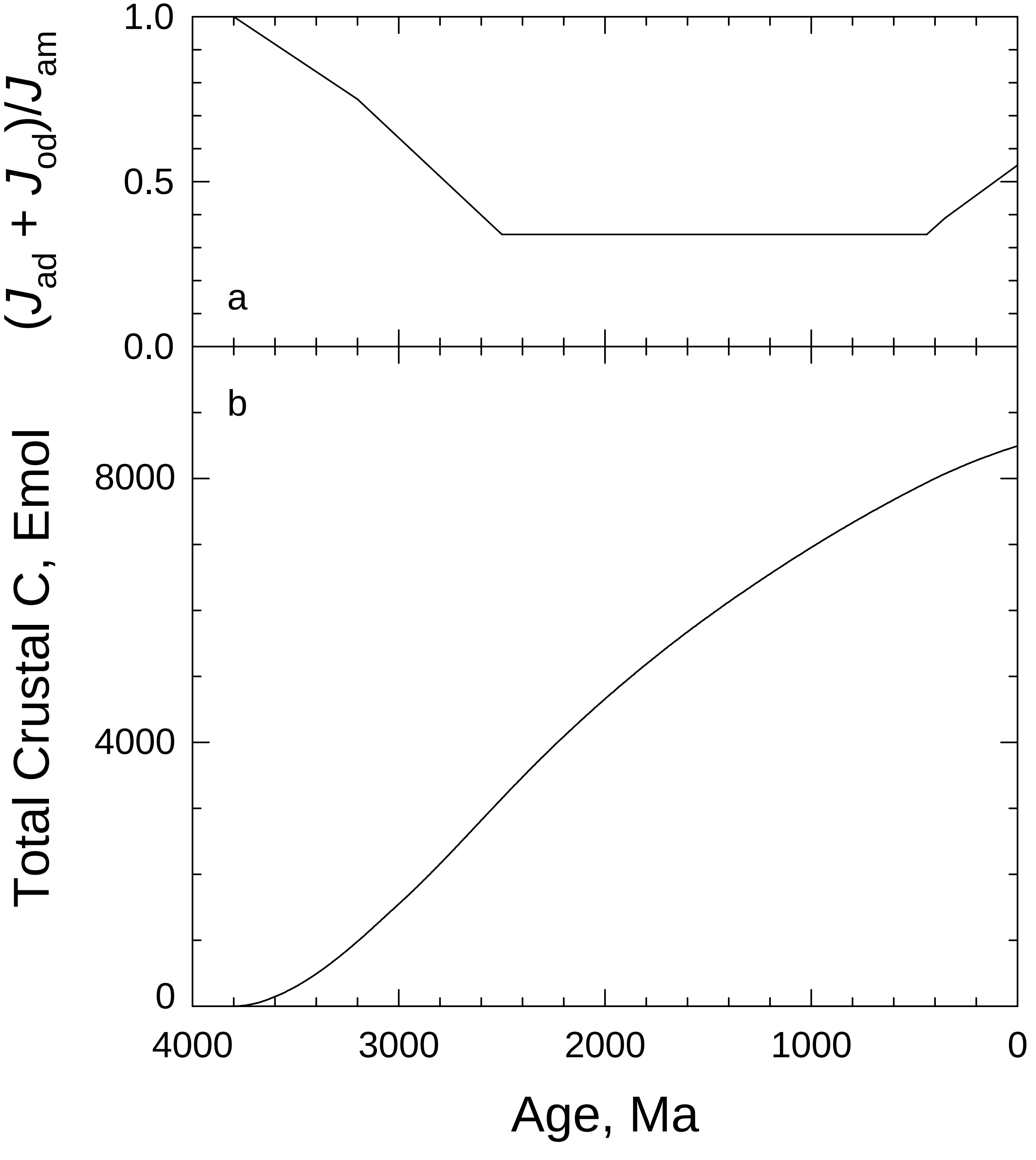
$$J_{os} - L_{Oxs} = L_{Redv} + J_{od} - L_{Oxd}$$

$$L_{Oxs} = \tfrac{1}{4}(\varphi_s - \varphi_{Mantle}) j_{Fe} + 2\, j_{SO4}$$

$$L_{Oxd} = \tfrac{1}{4}(\varphi_d - \varphi_{Mantle}) j_{Fe}$$

$$L_{Redv} = 2\, j_{CH4} + \tfrac{1}{2}\, j_{H2+SO2} + 2\, j_{H2S}$$

Figure 6



1.0
0.5
0.0
$(J_{ad} + J_{od})/J_{am}$
a
b
8000
4000
0
Total Crustal C, Emol
4000
3000
2000
1000
0
Age, Ma

Figure 7

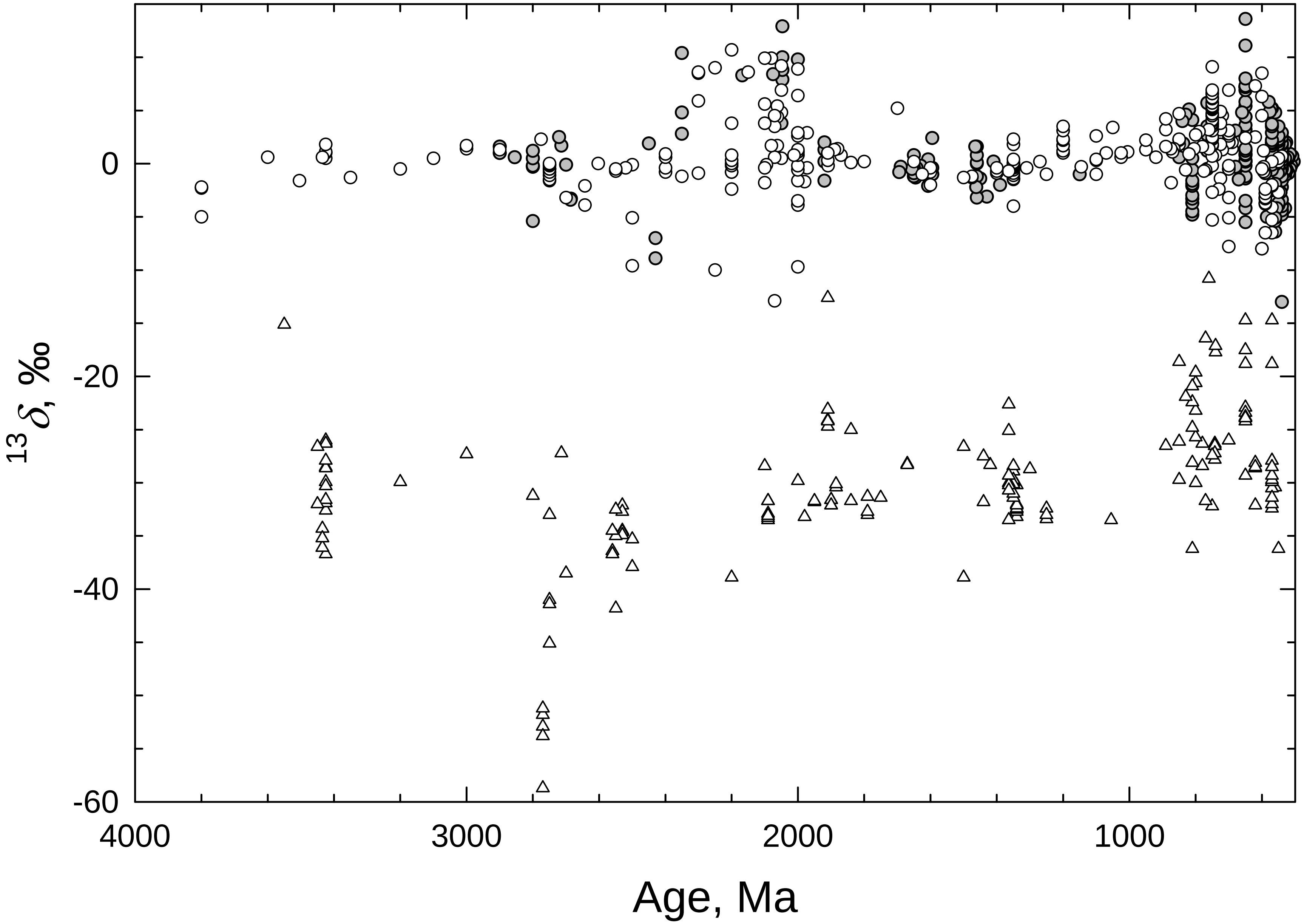


Figure 8

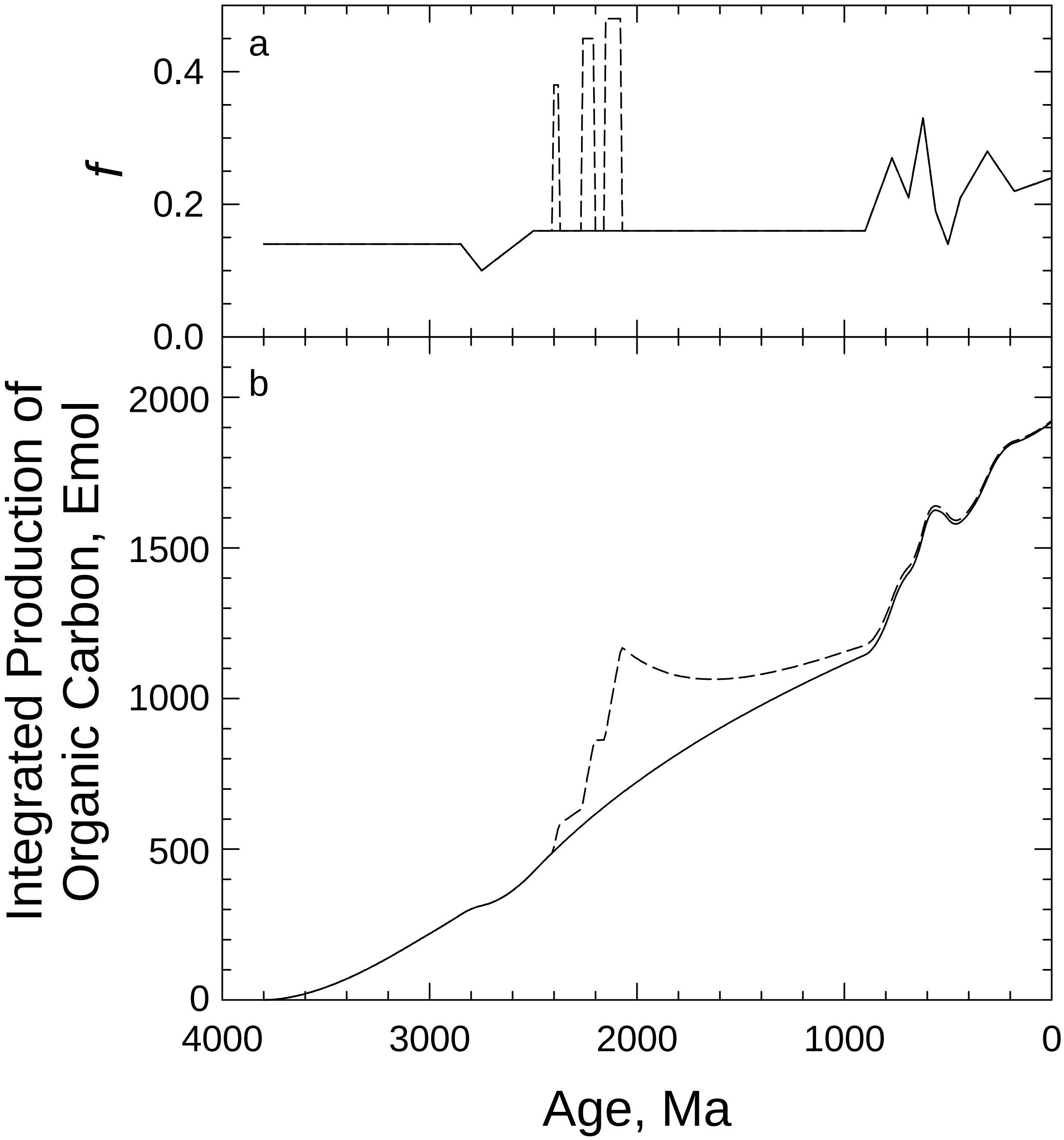

a
b
f
0.0
0.2
0.4
0
500
1000
1500
2000
Integrated Production of Organic Carbon, Emol
4000
3000
2000
1000
0
Age, Ma

Figure 9

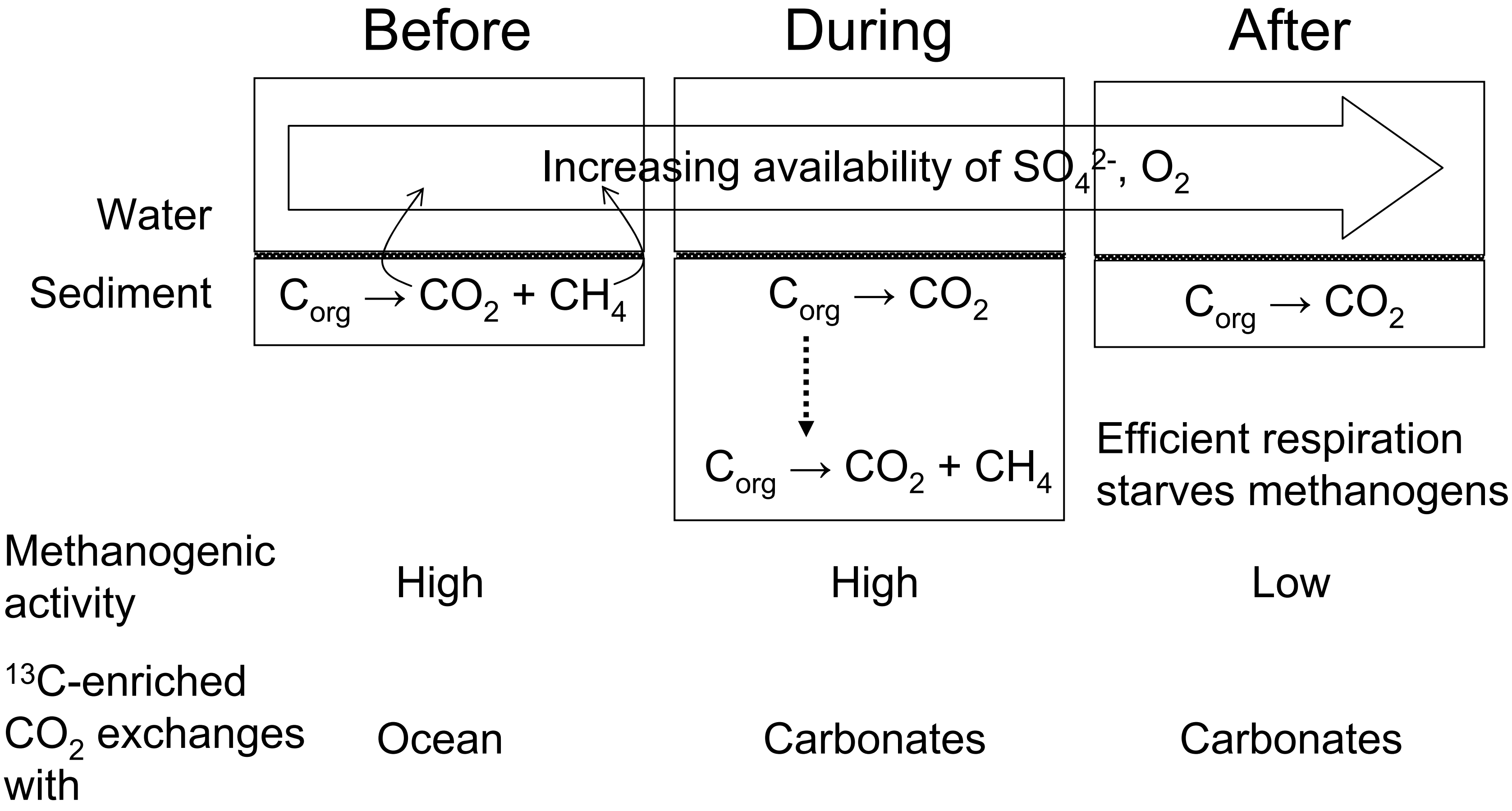

Before
During
After
Increasing availability of SO_4^{2-}, O_2
Water
Sediment
$C_{org} \rightarrow CO_2 + CH_4$
$C_{org} \rightarrow CO_2$
$C_{org} \rightarrow CO_2 + CH_4$
$C_{org} \rightarrow CO_2$
Efficient respiration starves methanogens
Methanogenic activity
High
High
Low
^{13}C-enriched CO_2 exchanges with
Ocean
Carbonates
Carbonates

Figure 10