

Fig. 16-1: Diagrammatic illustration of various components of the oxygen cycle. Oxygen is produced by photosynthesis. Most of the organic matter that is produced is then re-oxidized. Burial of organic matter leads to excess oxygen that is consumed by various reactions. Reduced Fe and S coming from hydrothermal vents and exposure of the continental crust are oxidized, as are the reduced gases coming out of volcanoes. Subduction recycles various molecules to Earth's interior. The oxidation state of sediments contains the record of these reactions through Earth history.

$\text{O}_2$  incorporated in oxidized species. This mass balance also provides us with two avenues to explore the history of oxygen, one through study of organic matter through time (the carbon cycle), which is the story of oxygen generation, and the other through study of the oxidized products (largely the Fe and S cycles), which is the story of oxygen consumption.

## Carbon: The Record of Oxygen Production

Reduced carbon resides in black shales, soils, coal, oil, and natural gas, resulting from billions of years of photosynthesis. This storage is what permits the high oxidation state of the planetary surface and the exis-

Table 16-1  
Reservoirs of carbon on Earth (in units of  $10^{18}$  moles)

Reservoir	Reduced (organic) C	Oxidized C	Total
Atmosphere	—	0.07	0.07
Biosphere	0.13	—	0.13
Hydrosphere	—	3.3	3.3
Deep-sea sediments	60	1300	1360
Continental margin sediments	>370	>1000	>1370
Sedimentary rocks	750	3500	4250
Other rocks	100	200–400(?)	300–500
Total surface reservoirs	~1250	~6100	~7350
Mantle	—	—	27000

Reduced carbon estimates are from Des Marais, *Rev. Mineral. Geochem.* 43 (2005):555–78.

tence of animal life that depends on it. If we were to somehow recover and burn all this organic matter, we would reverse 3 billion years of planetary evolution and return Earth to its reduced state where only primitive life is possible. The current distribution of organic and inorganic carbon in Earth reservoirs is shown in Table 16-1. Notice that the biosphere, living or recently living organic matter, is only a very small portion of total organic carbon, that total organic carbon is about 17% of total crustal carbon, and that the mantle is by far the largest carbon reservoir.

Tracking sources of  $O_2$  through time directly would require knowledge of how the mass of organic carbon has changed through time. This is an intractable problem because organic carbon resides in sediments, and these are rapidly recycled through Earth's history. So scientists have had to turn to an indirect method, where the rate of formation of organic carbon is inferred from measurements of carbon isotopes in carbonates formed from seawater and in ancient organic matter.

The reasoning behind this approach makes use of the contrast in carbon isotope ratios between organic carbon and carbonate carbon. The starting point is that we can measure the *average* carbon isotope ratio

of surface carbon reservoirs, and it turns out that this value is the same as the input to the system, which is carbon coming from the mantle. The mantle-derived carbon then becomes distributed by geological and biological processes to (inorganic) carbonate and organic carbon. As we learned in Chapter 13, biological processes that make the organic carbon preferentially incorporate  $^{12}\text{C}$ , the lighter of the two carbon isotopes, and the  $^{13}\text{C}/^{12}\text{C}$  ratio of organic carbon is about 3% lower than the ratio in inorganic carbon. The variations are reported as per mil differences relative to an arbitrary standard (per mil is parts per thousand, as compared to percent, which is parts per hundred). These differences are conventionally assigned the symbol  $\delta^{13}\text{C}$  ("del C 13"). For example, a value of  $\delta^{13}\text{C}$  of  $-30$  means the  $^{13}\text{C}/^{12}\text{C}$  ratio is 30 per mil lower than the standard value.

Mantle carbon has  $\delta^{13}\text{C}$  of  $\sim -5$ , which must always be the value of the total carbon in the system. At the same time, there will also always be the offset between organic and inorganic carbon, which is about 30 per mil. If all the carbon were in the form of inorganic carbon, then the inorganic carbon would have to have the mean value of  $-5$ . The first organic molecule to form would be offset 30 per mil lighter to  $-35$ . Or if all the carbon were only organic carbon, then the organic carbon value would be  $-5$  and the first inorganic carbon molecule would be offset to  $+25$ . The average is always  $-5$  and the offset is always 30, but the carbon isotope values of organic and inorganic carbon depend on the relative amounts of each (Fig. 16-2). Mathematically, the mass balance can be written as:

$$\delta^{13}\text{C}_{\text{or}} M_{\text{or}} + \delta^{13}\text{C}_{\text{ic}} M_{\text{ic}} = \delta^{13}\text{C}_{\text{T}} M_{\text{T}} \quad (16-5)$$

where  $M_{\text{T}}$  is the total mass of carbon,  $M_{\text{or}}$  is the mass of organic carbon and  $M_{\text{ic}}$  is the mass of inorganic carbon. Then  $M_{\text{T}} = M_{\text{or}} + M_{\text{ic}}$ . It is then possible to define a parameter, conventionally called  $f$ , which is the fraction of organic carbon to total carbon  $f = (M_{\text{or}}/M_{\text{T}})$ . Substituting terms, we obtain:

$$f = (\delta^{13}\text{C}_{\text{ic}} - \delta^{13}\text{C}_{\text{T}}) / (\delta^{13}\text{C}_{\text{ic}} - \delta^{13}\text{C}_{\text{or}}) \quad (16-6)$$

By measuring the  $\delta^{13}\text{C}$  values of organic and inorganic carbon in rocks of different ages,  $f$  can be estimated, permitting estimates of the proportion of organic to inorganic carbon through time (Fig. 16-2).

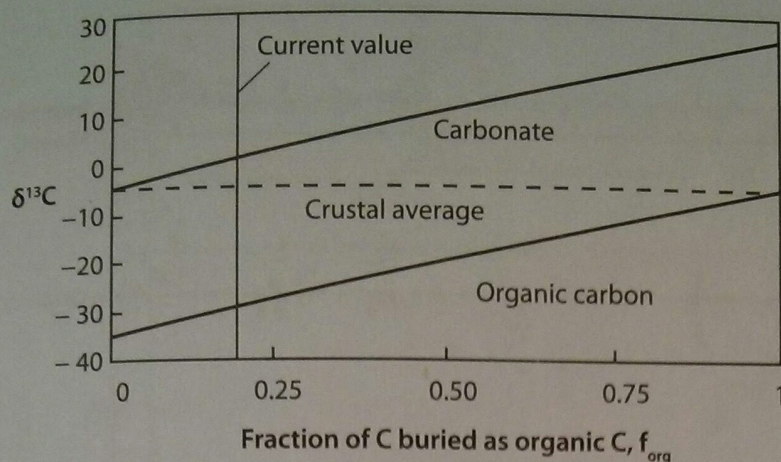


Fig. 16-2: Relationship between isotopic composition of carbonate carbon ( $\delta^{13}\text{C}_c$ ) and organic carbon ( $\delta^{13}\text{C}_{\text{org}}$ ) as a function of the fraction of carbon buried as organic matter. The offset between the two is always 30 per mil. The total carbon must always average  $-5$  per mil. The vertical line represents the current value for the global carbon cycle, and this value has remained remarkably constant over Earth's history. (Modified from Des Marais, *Reviews in Mineralogy and Geochemistry* v. 43, 555–78 (2001))

## Carbon: Evidence from the Rock Record

The principle behind a carbon isotope record is straightforward—to measure carbonate and organic matter of various ages that reflect seawater composition. In practice, there are many difficulties. Samples distributed over the various periods of Earth's history with preserved carbonates and preserved organic matter are necessary. While carbonates are fairly abundant in the geological record and sometimes well preserved, organic matter is rarer and more easily modified by metamorphic processes. There are also the difficulties that the two types of material are often in different rocks from different locations, so the record requires correlation of ages across different continents. These aspects make it difficult to obtain a reliable record and to know whether measurements at particular time intervals in the Precambrian are global in extent or reflect local conditions. With such questions about the data, interpretations have “wobble room.”

Despite the difficulties in detail, the long-term history of carbon isotopes tells a compelling story. The data for both organic and inorganic carbon are shown in Figure 16-3. The horizontal line provides a reference for the mantle value of  $\delta^{13}\text{C}$ . If no organic carbon were produced,

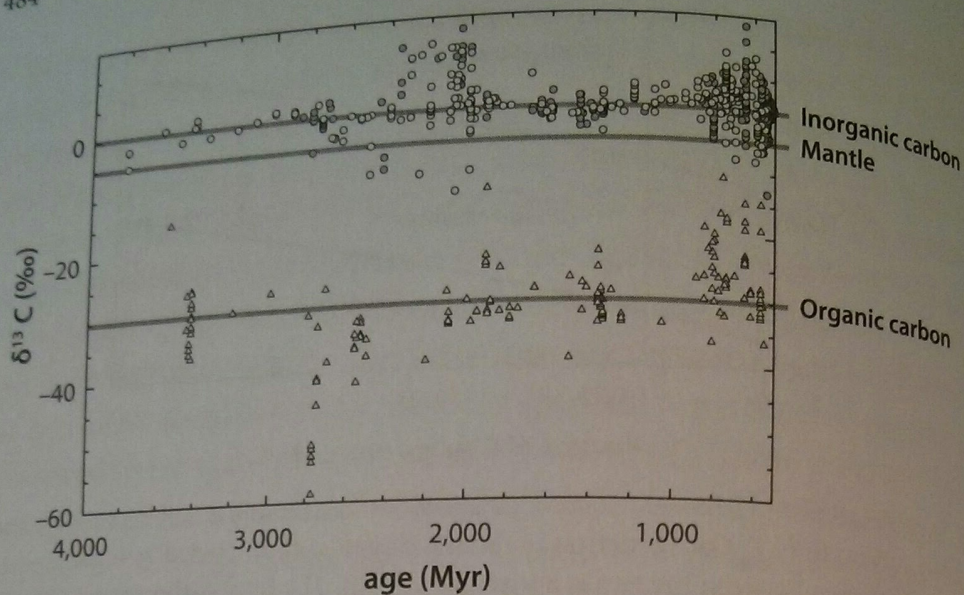


Fig. 16-3: Data for carbon isotopes from sediments over geological time. Open circles are carbonate (oxidized) carbon. Triangles are organic (reduced) carbon. Note the two periods of large variation in the carbon isotope composition of inorganic carbon near 2200 Ma and 800 to 600 Ma. (Adapted from Hayes and Waldbauer, *Phil. Trans. R. Soc. B.* 361 (2006):931–50)

we would expect carbonate carbon to have the same value as the mantle. As is apparent from the figure, throughout Earth's history carbonate carbon has had higher  $\delta^{13}\text{C}$  than the mantle, and the offset on average varies within a small range. Since mantle carbon is  $-5$ , carbonate carbon is about  $0$ , and organic carbon is about  $-30$ , this implies from Figure 16-2 that the carbonate carbon has made up about 80% of the active carbon reservoir, and inorganic carbon about 20%. This value inferred from carbon isotopes is essentially the same as total carbon balance seen in Table 16-1.

The contrast between carbonate carbon and organic carbon is not a simple constant, however, and while modern organic carbon varies around  $-30$  per mil, the sparse measurements of ancient organic carbon are lower. Simplifying and smoothing out the data by averaging leads to the variations in fraction of organic carbon through time shown in Figure 16-4. The scatter in the data preclude a definitive conclusion, but the data suggest a possible increase in proportion of organic matter from about 15% in the Archean to 20–25% today.

The carbonate isotope data also show two periods of increased variability, including excursions to much higher values of carbonate  $\delta^{13}\text{C}$ .

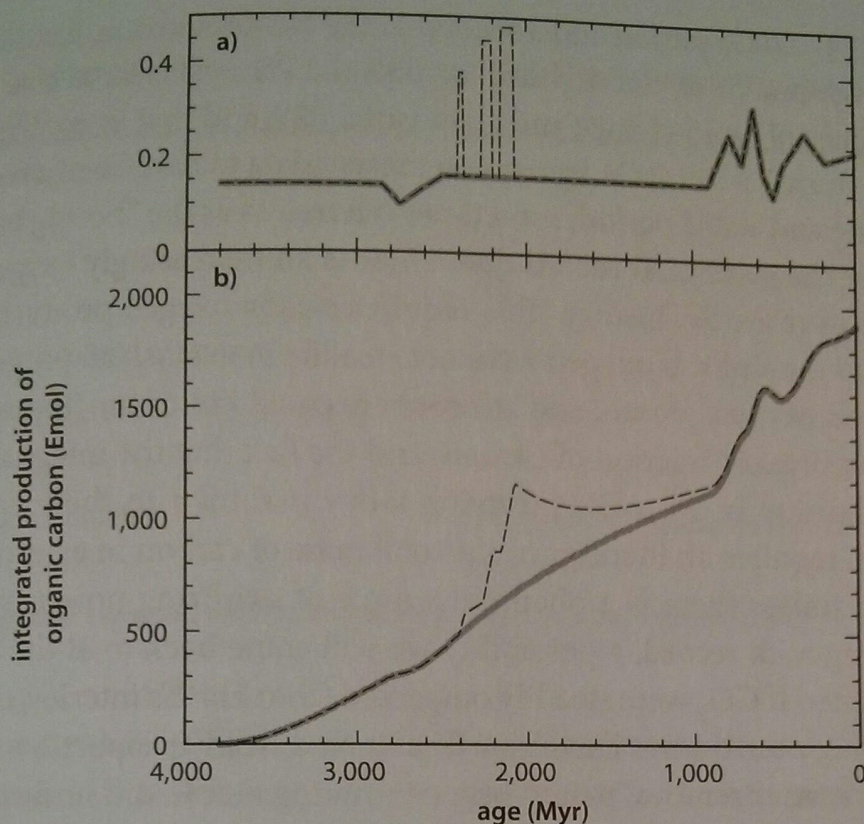


Fig. 16-4: Possible interpretation of smoothed data from figure 16-3. If  $\text{CO}_2$  is steadily outgassed from Earth's interior, then the total amount of carbon at the surface increases with time. The constant fraction of organic carbon (*top panel*) then means that total buried organic carbon also increases with time (*lower panel*). There may have been short time periods of increased fraction of organic carbon burial (indicated by the dashed lines). Since  $\text{O}_2$  production has a one-to-one relationship with organic carbon burial, the lower panel could also be viewed as the increase in oxidized molecules at the surface (largely oxidized Fe and S). (Modified after Hayes and Waldbauer (2006))

These occur between 2.4 and 2.0 Ga and 0.8 to 0.55 Ga. Taken at face value, these would suggest higher proportions of organic matter, and greater production of oxidizing power, during these two periods. If this were true in a simple way, however, we would expect to see in Figure 16-3 a smooth and globally uniform increase in carbonate  $\delta^{13}\text{C}$  values over these time periods and a corresponding increase in the  $\delta^{13}\text{C}$  of organic matter during the same time periods, and neither of these is evident. The "noise" and lack of correspondence of the organic and inorganic carbon records is problematic. Furthermore, these two time periods also show some negative  $\delta^{13}\text{C}$  excursions. Many workers have interpreted these data to indicate when oxygen rose in the atmosphere, with a first-step increase

in the 2.4–2.0 Ga period and a second in the Neoproterozoic just prior to the development of multicellular organisms. What is clear is that these were times of rapid change and great variability, and that in contrast, the period from 2.0 to 1.0 Ga appears on present data to have been a remarkably long and stable period, sometimes referred to as the “boring billion.”

What the geological record does show is an increasingly oxygenated surface over Earth’s history. This requires steady oxygen production in excess of the sinks. If oxygen were not steadily in excess, the progressive oxidation of crust, ocean, and atmosphere could not occur. Therefore, a constant organic fraction of carbon, and the fact that the integrated organic fraction in all rocks surviving today is similar to the long-term average, requires an increase in the total mass of carbon in external reservoirs, unless there is a phantom source of oxidizing power with no surviving rock record, a possibility we will come back to at the end of the chapter. If  $\text{CO}_2$  were steadily outgassed from Earth’s interior, thereby increasing over time at Earth’s surface, then a steady proportion of 20% organic matter removal would be a continuing flux to the surface, leading to a gradual increase in oxidizing power. It is not necessary to have periods of greater burial of organic matter to raise oxygen—oxygen is being produced all the time. A necessary consequence of this way of viewing the problem is that the total size of the organic matter reservoir would increase with time (as would the size of the carbonate reservoir). Determining the total carbon budget through Earth’s history is a difficult problem, however, because the rates of recycling and removal of carbon through subduction are poorly known, even for modern periods.

The data in Figure 16-3 also show a great deal of scatter and no clear correlation between variations in organic and inorganic carbon. The concept is clear. The data are noisy. Therefore the carbon isotopes provide important constraints and much food for thought about the rise of  $\text{O}_2$ , but do not provide definitive answers.

## Iron and Sulfur: The Record of Oxygen Consumption

The most important elements that track oxygen consumption are oxidized Fe and S. The rocks and seawater of Earth’s surface today contain