

Modeling Carbon Isotopes

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Introduction

In the introduction to this chapter, we saw that there was some very useful information contained in the changing ratio of ^{13}C to ^{12}C over time. In this section, we will explore the world of carbon isotopes in greater detail as we develop and experiment with a variety of models. Some of these models will enable us to better understand the relationship between burning fossil fuels and the atmospheric $^{13}\text{C}/^{12}\text{C}$ ratio, including how different possibilities for the "missing sink" affect the history of in the atmospheric $^{13}\text{C}/^{12}\text{C}$ ratio. A more complex model will be used as a means for understanding what happened to the carbon cycle in the oceans during the crisis at the Cretaceous-Tertiary boundary, 65 million years ago, when Earth was hit by a very large asteroid, producing some very dramatic, catastrophic changes to the climate.

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Isotopes of Carbon

As mentioned earlier, there are a variety of naturally-occurring isotopes of carbon. These isotopes are characterized by differing atomic weights resulting from varying numbers of neutrons in the atomic nuclei. The relative abundances of these isotopes are given below:

^{12}C 98.89%

^{13}C 1.11%

^{14}C 1E-10%

^{12}C and ^{13}C are both stable isotopes, meaning that unlike their radioactive cohort, ^{14}C , they do not undergo radioactive decay. ^{14}C is constantly being produced in the atmosphere as nitrogen atoms are bombarded by high-energy solar radiation, but it is also being destroyed (converted to ^{12}C) as it undergoes radioactive decay. ^{14}C has also been produced during atmospheric nuclear explosions, most of which occurred in the early 1960s. The production of ^{14}C is also dependent on things like the variations in solar output and the strength of the Earth's magnetic field, which acts to shield out the radiation that produces ^{14}C .

Isotopic ratios are typically represented as deviations relative to a standard ratio that occurs in some "standard" material. The format for reporting these ratios is shown in the equation below:

$$\delta^{13}\text{C} = \left(\frac{\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{sample}} - \left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{standard}}}{\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{standard}}} \right) \times 1000$$

This is simply the fractional difference between a sample and the standard, only here, it is actually a per mil (‰) difference rather than a percent (%) difference since the values tend to be so small. Looking at the above equation, we can see that if a sample has a greater proportion of the heavier isotope of carbon, ^{13}C , then it will have a positive $\delta^{13}\text{C}$ value and if it is depleted in the heavier isotope, then it will have a negative $\delta^{13}\text{C}$ value. The standard was originally the carbon contained in calcite from fossils called belemnites from a particular limestone called the Pee Dee Formation (abbreviated as PDB).

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Fractionation of Isotopes

Earlier in this chapter, we mentioned that the carbon released from burning fossil fuels has a lower $\delta^{13}\text{C}$ (-25 to -20‰) than the atmosphere (-8‰). Why is this so? A partial explanation is that fossil fuels are derived from a combination of terrestrial and marine organic material, and if we look at the carbon isotope values in those material today, we see that they have $\delta^{13}\text{C}$ values of around -25‰ to -20‰. But then the question becomes: Why are the $\delta^{13}\text{C}$ values of modern organic matter so different from the atmosphere? This brings us to the underlying explanation -- the process of photosynthesis favors the lighter form of carbon. Photosynthesis, along with a few other processes, lead to variations in carbon isotope ratios. These processes are sometimes called isotope fractionation processes, which turn out to be very useful in helping us to decipher the past behavior of the carbon cycle.

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Natural Variations in Carbon Isotope Ratios

The various fractionation processes lead to the natural variations shown in Figure 7.17.

Variations in Carbon Isotopes

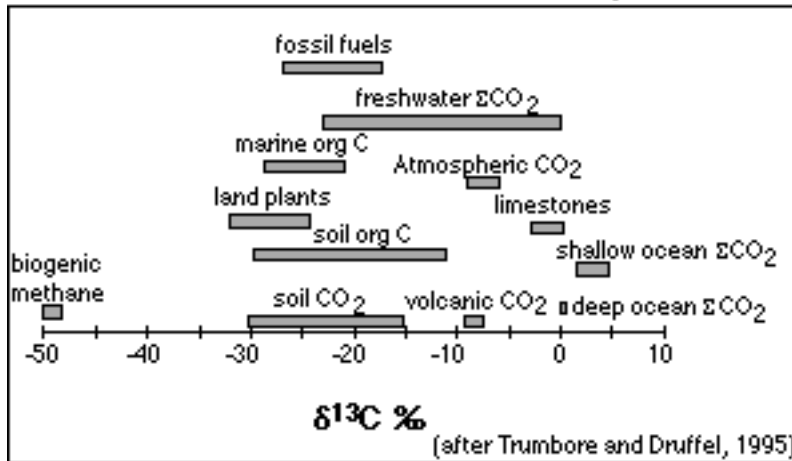


Figure 7.17 Different pools of carbon and different forms of carbon are characterized by widely varying $\delta^{13}\text{C} \%$ values, as a result of different fractionation processes. Methane can be produced in two main ways — biogenically (by microbes), and through the thermal breakdown of marine organic matter deposited in sedimentary rocks. The biogenic process is a multi-step process with each step involving a preference for lighter carbon, making the methane exceptionally light.

There are a few features in this figure that are worth discussing. One is that land plants, soil organic matter, soil CO₂, marine organic matter, and fossil fuels all tend to hover in the -20 to -30‰ range. This reflects the fact that photosynthesis -- on land or in the sea -- always takes more of the lighter carbon from the mix of available CO₂. This means that the carbon fixed by plants will always have a $\delta^{13}\text{C}$ value that is less than that of the source CO₂. This shift is generally in the range of -20 to -30‰, depending on a variety of environmental factors, and the details of the process of photosynthesis. This fractionation or discrimination involved with photosynthesis explains several other features of Figure 7.17. The shallow oceans are more positive than the deeper oceans because planktonic organisms take the lighter carbon out of the shallow water to make everything but their shells. Removing the light carbon will naturally leave the sea water depleted in the lighter carbon, so the sea water itself becomes more positive. When these organisms die, they sink to the deeper parts of the oceans, where their organic remains are largely decomposed, returning the carbon to the water, causing the deeper waters to be less positive than the surface waters. The difference between the surface $\delta^{13}\text{C}$ and the deep ocean $\delta^{13}\text{C}$ is a measure of the efficiency of the biologic pump -- this difference can be measured by studying the shells of surface-dwellers and bottom-dwellers that are preserved in deep-sea sediments. Limestones will tend to sample and preserve the carbon isotopic signature of the ocean water where the majority of the organisms whose shells make up the limestone were living, with perhaps a small effect from the incorporation of a bit of organic material. The extreme outlier in above figure is methane, which is extremely negative as a result of being the end-product of several steps carried out by microbes wherein each step involves a preference for the lighter form of carbon.

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Changes in Isotopic Ratios of Reservoirs

To make a model that monitors the isotopic ratio of carbon in various reservoirs, we need to develop some equations, but first, it will help to solidify a few very simple ideas by considering a couple of examples -- simple thought experiments.

Imagine that we have a reservoir of carbon that has an initial $^{13}\text{C}/^{12}\text{C}$ ratio and then we add new carbon with the same ratio as the carbon that was already in the reservoir. The total amount of carbon will have increased, but the ratio of carbon isotopes will remain the same. Next, imagine what happens if we add carbon with a smaller ratio of $^{13}\text{C}/^{12}\text{C}$ -- the amount of carbon once again increases, but the $^{13}\text{C}/^{12}\text{C}$ ratio of reservoir will have decreased. How about if we remove carbon from the reservoir, and we discriminate in this removal such that the carbon taken away has a smaller $^{13}\text{C}/^{12}\text{C}$ ratio than the overall reservoir? In this case, the amount of carbon in the reservoir will obviously decrease, but the $^{13}\text{C}/^{12}\text{C}$ ratio in the reservoir will increase.

What we need for the purposes of a model is a general equation that will calculate the changes in the isotopic values for reservoirs as a function of the amount of carbon added or subtracted and the ratio of that carbon relative to the carbon in reservoir. We start by considering a reservoir called M that has an inflow F_i and an outflow F_o . The rate of change of the reservoir is just:

$$\frac{dM}{dt} = F_i - F_o \quad (1)$$

If the inflow and outflow transfer carbon with specific $\delta^{13}\text{C}$ values, δ_i and δ_o , and if we know the starting $\delta^{13}\text{C}$ for the reservoir, δ_M , we can write a similar equation to the above that incorporates these isotopic ratios:

$$\frac{dM\delta_M}{dt} = F_i\delta_i - F_o\delta_o \quad (2)$$

But what we're really after is an equation that tells us how δ_M changes with time, so we need to deconstruct the above equation (2). We apply the product rule of calculus to the above, giving:

$$\delta_M \frac{dM}{dt} + M \frac{d\delta_M}{dt} = F_i\delta_i - F_o\delta_o \quad (3),$$

and then we rearrange things in (3) to get:

$$\frac{d\delta_M}{dt} = \frac{1}{M} \left(F_i\delta_i - F_o\delta_o - \delta_M \frac{dM}{dt} \right) \quad (4).$$

Then we substitute (1) into (4) to get the following:

$$\frac{d\delta_M}{dt} = \frac{1}{M} (F_i \delta_i - F_o \delta_o - \delta_M (F_i - F_o)) \quad (5)$$

which can be simplified by rearranging terms to give us our final equation:

$$\frac{d\delta_M}{dt} = \frac{1}{M} (F_i (\delta_i - \delta_M) - F_o (\delta_o - \delta_M)) \quad (6).$$

This final equation then is essentially what gets entered as the equation for a flow that feeds in and out of a reservoir that is the isotopic ratio of the carbon contained in another reservoir. This is a rather unusual kind of quantity to keep track of in a reservoir -- not as intuitive as the mass of carbon in the atmosphere for instance.

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Construction of a Simple Atmospheric $\delta^{13}\text{C}$ Model

Now it is time to apply what we learned in the last section in the form of a very simple model that represents a small portion of the carbon cycle. We will model only the atmospheric reservoir and only one flow into the reservoir -- the carbon emitted from burning fossil fuels. Our goal here is to represent the historical fossil fuel emissions and their effect on the atmospheric $\delta^{13}\text{C}$ under some very simple assumptions. We assume that the atmosphere started out with a $\delta^{13}\text{C}$ of -6, which is known from studying tree rings and also from ice core measurements. The $\delta^{13}\text{C}$ of fossil fuels varies (see above figure) with an average of around -22‰, and the history of emissions is reasonably well known - it is included here as a graphical function of time, beginning in 1860 and ending in 1990. The structure of our model is shown in Figure 7.18. Note that the flow connected to the $\delta^{13}\text{C}$ reservoir is a bi-flow rather than a uniflow — this allows for an increase or a decrease in the reservoir quantity, while a uniflow would only allow for an increase or a decrease (but not both).

Very Simple Atmospheric $\delta^{13}\text{C}$ Model

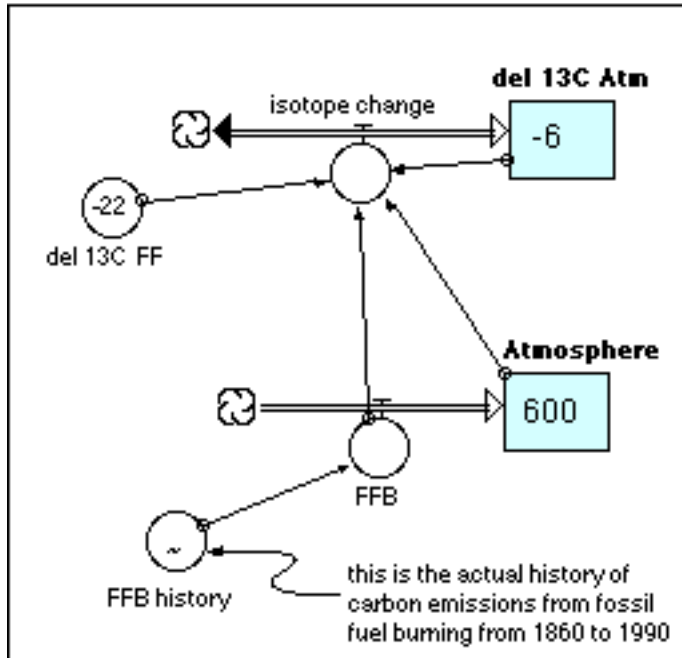


Figure 7.18 An elementary first model of atmospheric carbon isotopes consists of a very simplistic model keeping track of the mass of carbon in the atmosphere [below] and linked model that keeps track of the isotopic ratio of the carbon in the atmosphere.

The equations that lie beneath this model structure are listed below. Note that there is a rather lengthy listing for the FFB (fossil fuel burning) history -- this is the most detailed resolution available and it means that we have to adjust the beginning and ending times of our simulations (in the Time Specs dialog box) to go from 1860 to 1990. Because of the large number of data points here, I suggest that you load this model, which includes the pre-made graph for FFB history, from the disk that accompanies this book.

Equations for Very Simple Atmospheric $\delta^{13}\text{C}$ Model

Reservoirs:

INIT Atmosphere = 600 {Gt C}
 INIT del_13C_Atm = -6 {pre-industrial del13C}

Flows:

FFB = FFB_history {FFB stands for fossil fuel burning}
 isotope_change = (FFB*(del_13C_FF-del_13C_Atm))/Atmosphere

Converters:

del_13C_FF = -22 {del13C of fossil fuels}
 FFB_history = GRAPH(time)
 (1860, 0.0933), (1861, 0.0987), (1862, 0.0984), (1863, 0.106), (1864, 0.115), (1865, 0.122), (1866, 0.129), (1867, 0.138), (1868, 0.137), (1869, 0.142), (1870, 0.145), (1871, 0.162), (1872, 0.176), (1873, 0.188), (1874, 0.184), (1875, 0.189), (1876, 0.192), (1877, 0.196), (1878, 0.197), (1879, 0.208), (1880, 0.227), (1881, 0.244), (1882, 0.263), (1883, 0.28), (1884, 0.282), (1885, 0.276), (1886, 0.279), (1887, 0.298), (1888, 0.322), (1889, 0.329), (1890, 0.35), (1891,

0.365), (1892, 0.369), (1893, 0.362), (1894, 0.377), (1895, 0.399), (1896, 0.412), (1897, 0.431), (1898, 0.455), (1899, 0.497), (1900, 0.525), (1901, 0.54), (1902, 0.553), (1903, 0.606), (1904, 0.613), (1905, 0.647), (1906, 0.696), (1907, 0.771), (1908, 0.737), (1909, 0.769), (1910, 0.805), (1911, 0.822), (1912, 0.866), (1913, 0.929), (1914, 0.838), (1915, 0.831), (1916, 0.895), (1917, 0.945), (1918, 0.932), (1919, 0.829), (1920, 0.959), (1921, 0.828), (1922, 0.891), (1923, 1.01), (1924, 0.999), (1925, 1.01), (1926, 1.01), (1927, 1.10), (1928, 1.09), (1929, 1.17), (1930, 1.08), (1931, 0.968), (1932, 0.874), (1933, 0.919), (1934, 0.997), (1935, 1.03), (1936, 1.15), (1937, 1.23), (1938, 1.16), (1939, 1.23), (1940, 1.30), (1941, 1.34), (1942, 1.33), (1943, 1.36), (1944, 1.35), (1945, 1.20), (1946, 1.27), (1947, 1.42), (1948, 1.52), (1949, 1.49), (1950, 1.64), (1951, 1.77), (1952, 1.80), (1953, 1.85), (1954, 1.87), (1955, 2.05), (1956, 2.19), (1957, 2.28), (1958, 2.34), (1959, 2.47), (1960, 2.59), (1961, 2.60), (1962, 2.71), (1963, 2.85), (1964, 3.02), (1965, 3.15), (1966, 3.31), (1967, 3.42), (1968, 3.60), (1969, 3.81), (1970, 4.08), (1971, 4.24), (1972, 4.40), (1973, 4.64), (1974, 4.65), (1975, 4.62), (1976, 4.89), (1977, 5.03), (1978, 5.08), (1979, 5.36), (1980, 5.29), (1981, 5.12), (1982, 5.08), (1983, 5.07), (1984, 5.24), (1985, 5.41), (1986, 5.60), (1987, 5.73), (1988, 5.95), (1989, 6.07), (1990, 6.10)

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Experiments

1. Preliminary Effects of Fossil Fuel Emissions

We will run the first experiment with the basic model, described above, to see how the $\delta^{13}\text{C}$ of the atmosphere will change, recognizing that this is a fairly primitive model at this point. Set the program to run from 1860 to 1990 with a time step of 1.0, using the Runge-Kutta 2 integration method. Before running the model, pause to make a prediction. What will happen? How much (and in what direction) will the atmospheric $\delta^{13}\text{C}$ change? Analyze the results in the form of a graph that shows $\delta^{13}\text{C}$ for the atmosphere, the total carbon in the atmospheric reservoir, and the FFB flow. How realistic are the results? You can consider the results in a qualitative sense and also in a quantitative sense by comparing the actual record, seen in Figure 7.02, with the model output.

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2. Reducing FFB by 50%

Part of the problem with our first model is that all of the carbon produced by FFB stays in the atmosphere. In reality, only about 50% seems to be accumulating. Let's assume that, over the course of the last 130 years, this 50% retention figure has remained the same. We can implement this change by simply modifying the FFB flow so that it is equal to $0.5 * \text{FFB_history}$. It should be fairly easy to predict the outcome of this change. How do the results compare with the known record of atmospheric $\delta^{13}\text{C}$? In making this change, we are implicitly assuming that the mechanisms that remove some of the carbon from the atmosphere remove carbon with the same $\delta^{13}\text{C}$ value as the carbon produced by fossil fuel burning. This assumption is probably wrong and we'll address this issue in the next experiment.

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3. Adding Outflows -- Exploring the Problem of the Missing Sink

Now we'll make another increase in complexity by adding two outflows that represent the main sinks for atmospheric carbon -- uptake by the ocean and photosynthesis by land plants. Together, we will assume that these flows account for 60% of the carbon released by FFB. Both of these processes also involve an isotopic fractionation -- they prefer the lighter form of carbon. Photosynthesis, as we mentioned before, involves a -25‰ shift or fractionation, which means that the carbon it extracts from the atmosphere is always 25‰ lighter than the $\delta^{13}\text{C}$ of the atmosphere. The transfer of carbon from the atmosphere to the sea involves a smaller fractionation, of around -2‰, again showing a preference for the lighter form of carbon, which can diffuse across the air-sea boundary more easily. This is complicated by the fact that the reverse process -- the transfer of carbon from the sea to the air -- involves a different fractionation (around -9 to -10‰). But in our model here, the ocean will not be permitted to give carbon to the atmosphere, so we will ignore this process.

The question now is how to incorporate these carbon uptake processes that involve fractionation. Let's begin by examining our basic equation that we developed above;

$$\frac{\delta_M}{dt} = \frac{1}{M} (F_i(\delta_i - \delta_M) - F_o(\delta_o - \delta_M)) \quad (6).$$

Here, the outflow process is represented by F_o , and the carbon it removes is characterized by a ratio of δ_o . But, in this case, δ_o is not a fixed value -- it depends on δ_M , the ratio of carbon in the reservoir that is being drained. In other words,

$$\delta_o = \delta_M - \Delta_o \quad (7)$$

where Δ_o is the isotopic shift (or fractionation), such as -25‰ for photosynthesis. Then if we plug (7) into (6), we end up with:

$$\frac{\delta_M}{dt} = \frac{1}{M} (F_i(\delta_i - \delta_M) - F_o\Delta_o) \quad (8),$$

which can be expanded to include the effects of two outflow processes with separate isotopic shifts, to give us the final equation we need for our enhanced model:

$$\frac{\delta_M}{dt} = \frac{1}{M} (F_i(\delta_i - \delta_M) - F_{o1}\Delta_{o1} - F_{o2}\Delta_{o2}) \quad (9),$$

Incorporating these changes leads to a revision of the model, shown in Figure 7.19. Below, I list the equations (minus the graph of the history of fossil fuel burning) of this modified model.

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An Improved Atmospheric $\delta^{13}\text{C}$ Model

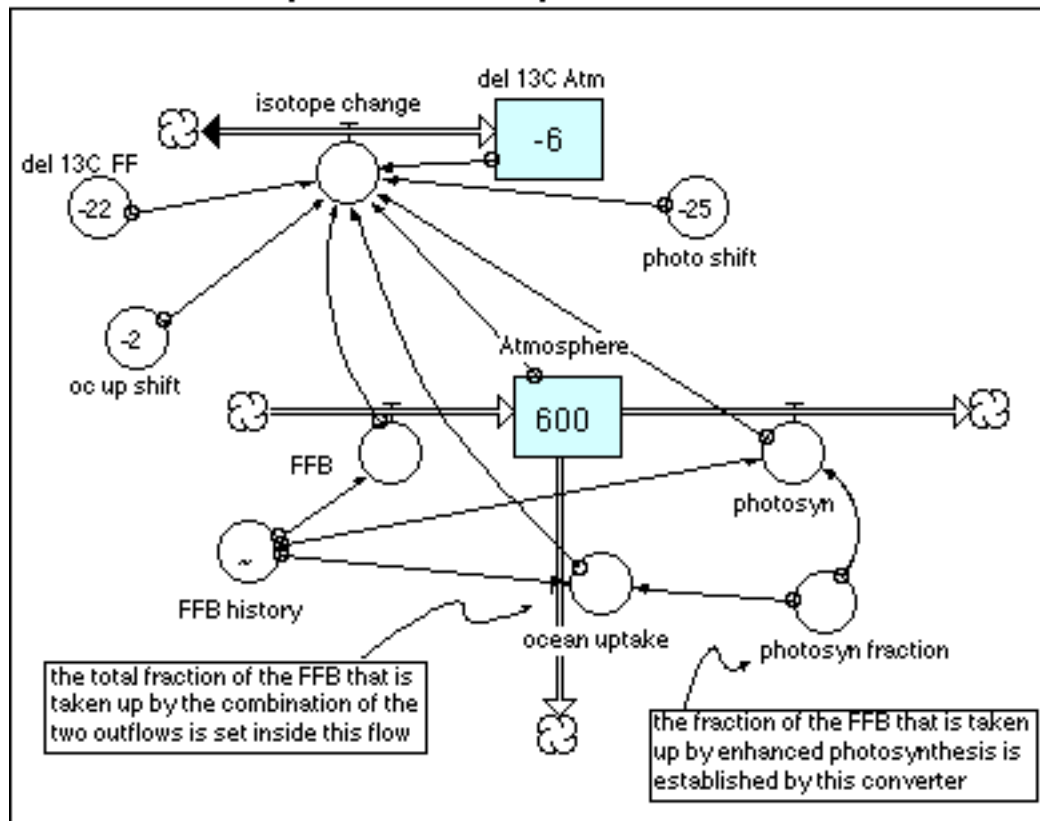


Figure 7.19 An improved (yet still very simple) model of atmospheric carbon isotopes contains two outflows that represent sinks for the anthropogenic emissions. The outflows collectively take up 50% of the emissions and the model is set up to alter the relative proportions of these two outflows.

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• Equations for an Improved Atmospheric $\delta^{13}\text{C}$ Model

Reservoirs:

INIT Atmosphere = 600 {Gt C}
 INIT del_13C_Atm = -6 {pre-industrial del13C}

Flows:

FFB = FFB_history {FFB stands for fossil fuel burning}
 photosyn = FFB_history*photosyn_fraction
 ocean_uptake = FFB_history*(.5-photosyn_fraction)
 isotope_change = (1/Atmosphere)*((FFB*(del_13C_FF-del_13C_Atm))-((photosyn*photo_shift)-(ocean_uptake*oc_up_shift))

Converters:

del_13C_FF = -22 {del13C of fossil fuels}
 photo_shift = -25 {isotopic shift for photosynthesis}
 oc_up_shift = -2 {isotopic shift for air-to-sea transfer}
 photosyn_fraction = .25 {fraction of FFB taken up by enhanced photosynthesis}
 FFB_history = same as first model

With this improved, more realistic model, we can venture into the realm of paying closer attention to the quantitative results of the model, although we must remember that we are still dealing with only a reduced version of the global carbon cycle. This model provides a means of exploring some possible solutions to one of the major questions concerning the global carbon cycle -- the problem of the "missing sink". At the present time, we cannot really balance the budget of the carbon cycle. We know that about half of the FFB emissions are accumulating in the atmosphere, and the available evidence indicates that around 20% to 30% is being swallowed up by the oceans, leaving another 20% to 30% that must be going somewhere -- into the "missing sink". Most people assume that the terrestrial part of the carbon cycle makes up the missing sink, but it is extremely difficult to accurately measure, on a global scale, where this extra carbon is going. With this model, we can explore a couple of possibilities, outlined below.

1) What if all the excess carbon -- 50% of FFB -- is taken up by the oceans with none of it going into the terrestrial biosphere? What are the implications for the atmospheric $\delta^{13}\text{C}$? Do the observations rule out this possibility? Can we alter the ocean uptake isotopic shift so that the model results come into close agreement with the observations? (We're hoping to end up in 1990 with an atmospheric $\delta^{13}\text{C}$ of around -8 to -8.5.) How much do you have to change this isotopic shift to get the model to fit the results?

• 2) What if all the excess --50% of FFB -- carbon is taken up by the terrestrial part of the carbon cycle? What are the implications for the atmospheric $\delta^{13}\text{C}$? Do the observations rule out this possibility? Can we alter the photosynthesis isotopic shift so that the model results come into close agreement with the observations? How much do you have to change this isotopic shift to get the model to fit the results?

3) If we preserve the isotopic shifts at -2‰ and -25‰, what mix of ocean uptake and photosynthetic uptake gives us an atmospheric $\delta^{13}\text{C}$ of around -8 to -8.5 by the year 1990?

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Exploring the Dynamics of the Cretaceous-Tertiary Crisis

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Background on the K/T Mass Extinction

In this section, we will apply many of the same ideas developed above to investigate one of the most important events in Earth's history -- the mass extinction that occurred at the Cretaceous-Tertiary (K/T) boundary, 65 million years ago. At this time, something like 50% of the known genera (and perhaps 80% at the species level) of organisms became extinct, including the dinosaurs. The extinction of the dinosaurs is an interesting case since, as a group, they had done very well for a very long time -- they were a great success story, and then they disappeared. But more importantly for the biosphere and the whole Earth system, many other organisms, including most species of plankton, also became extinct, thus dealing a serious blow to food webs in many ecosystems.

This mass extinction effectively "cleared the slate" biologically, and in the aftermath, the few survivors were faced with a very different world, one with all sorts of possibilities and unoccupied niches. All of this opportunity is thought to have encouraged prolific speciation -- the evolution of new life forms. Mammals had been around in small numbers for many millions of years before the K/T boundary, but they never seemed to be capable of really establishing themselves in a wide variety of niches. But, some of the mammals survived the K/T mass extinction and in the aftermath, they underwent an evolutionary explosion with many new species evolving, one of which eventually led to us. So, in a sense, part of the reason we are here today is that mammals happened to survive the K/T mass extinction.

Perhaps the central question in this whole matter is: what caused this mass extinction? Understanding the time over which the extinctions took place is another key question and it is this question that ultimately led to our present understanding of what caused this crisis. Before 1980, this matter of the cause received plenty of attention, but most of the ideas were highly speculative -- no one had really found any good hard evidence to support any hypothesis.

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Iridium and the Impact Hypothesis

Around 1980, Walter Alvarez and some colleagues were studying a sequence of rocks in Italy, studying the reversals of the magnetic field that were recorded in these rocks. Walter happened to notice that in these rocks, which were deposited on the floor of a deep sea, that the K/T boundary was marked by the very sudden disappearance of planktonic fossils. A thin clay layer, 3 cm thick, separated the Cretaceous from the Tertiary and just below this clay layer, there were plenty of Cretaceous plankton, so the extinction looked to be very abrupt. But, knowing that a bedding plane can sometimes represent a huge gap in time, Alvarez wondered if there was some way of measuring how much time the clay layer represented -- that would provide a powerful constraint on the length of time over which the extinction took place. Walter's father, a Nobel laureate physicist, came up with an ingenious idea -- measure the concentration of iridium in the layer. Iridium is very rare at the surface of the Earth (most of Earth's allotment of iridium

is deep in the core), but it does fall to the surface as dust particles from micro-meteorites that burn up in our atmosphere. This rate of fall-out is known, and so if you know the concentration, you can figure out how much time a layer of sediment represents.

When they measured the iridium concentration of this clay layer, they found that it was unbelievably high -- they had the magnetic reversals to provide an upper limit on the length of time the clay layer could represent, and the iridium seemed to exceed this upper limit by a wide margin. Puzzled and intrigued, they sought another explanation for the high concentration of iridium and eventually came up with the idea that the iridium came from a very large asteroid that hit the Earth and effectively delivered a huge slug of iridium all at once. Knowing the average concentration of iridium in asteroids, they calculated that the asteroid was 10 km in diameter. Asteroids travel at a velocity of around 15 km/sec, which, combined with the mass of the object, would produce an explosion on impact that exceeds the explosive energy of all the nuclear weapons on earth by a factor of about 10,000! This explosion is unimaginably large and it would have blown a huge crater in the Earth's surface, blasting the vaporized, pulverized impactor and target rock high above the troposphere, quickly forming a dense, opaque blanket over the Earth. This impact cloud would have blocked the sunlight for at least several months, plunging the Earth into an extremely cold state and halting photosynthesis, which is the basis of the food chain. Hot droplets of molten rock would have rained down on the surface, igniting fires. Shock-heating of the atmosphere would have produced rainfall with an acidity approaching battery acid at least in the region around the impact.

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Testing the Impact Hypothesis

What a disaster! And what a story to come out of such a thin, unassuming clay layer. But did it really happen? Are there other pieces of evidence that can support or refute this hypothesis? One prediction is that this iridium-bearing layer should be found all over the globe, and it has in fact been located in several hundred localities, spanning the globe. Another prediction is that there should be small fragments of the target rock, tiny sand-sized particles that were blasted from the impact site and settled into the same clay layer with the iridium. The origin of these sand grains could be determined by the presence of rare features that form in quartz crystals as a result of a shock wave passing through rocks. The only natural way of forming shock-deformed quartz is in an asteroid impact, so these shocked quartz grains are extremely helpful in testing the impact hypothesis. As it turns out, these shocked quartz grains do occur in the clay layer. Another thing found in the clay layer is soot that is thought to be from huge fires on the continents; the amount of soot implies that up to one-half of the plant material on land burned at this time.

In addition, the impact hypothesis predicts that we might be able to locate the actual impact crater, which could then be connected based on age and chemistry to the materials found in the clay layer. And, once again, it turns out that such a crater has been found, buried beneath hundreds of meters of younger sediment in the Yucatan Peninsula of Mexico, at a site called Chicxulub.

Over the last 10 years, there has been a nearly unprecedented frenzy of activity investigating this hypothesis and it seems to have passed all the test with flying colors, and as a result, the vast majority of geologists now favor this hypothesis as the best explanation for what caused the mass extinctions at the K/T boundary. The realization that our Earth has suffered such catastrophes came a shock (pardon the pun) to geologists who previously had been conditioned to think of gradual, slow changes occurring over vast spans of time. We now appreciate that dramatic, rapid, even catastrophic changes do occur and they can be among the most important events in the history of the Earth.

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Modeling the K/T Impact Crisis

The K/T crisis presents some very interesting opportunities for understanding how the Earth system responds to very extreme perturbations. Does it recover and return to a steady state? The fact that we exist tells us that it certainly does recover, but how quickly?

There are several approaches that we can take to understand how the various parts of the system respond to this kind of a crisis. We could investigate the effects using our simple climate models developed an earlier chapter on climate modeling. Or we could investigate it by altering the global carbon cycle that we developed in the first section of this chapter. I encourage you to return to those models and think about how you would modify them to represent the changes imposed by the dust cloud of the impact. One obstacle to this modeling approach is that we would need to make some assumptions about how the biosphere reacted to the crisis. For instance, how long did photosynthesis stop? How greatly was the ocean biologic pump affected, and for how long? To get at some of these questions, we can use a model of carbon isotopes in the ocean-atmosphere system to help us interpret the meaning of the measured carbon isotopes from planktonic and benthonic (bottom-dwelling) organisms. This will help us understand what the effects of the impact actually were on the ocean system.

First, let's look at the actual data that has been acquired from deep-sea sediments spanning this event. Figure 7.20 shows the general story, as told by organisms living in the surface waters and the bottom of the oceans. These organisms make their shells out of calcite and the calcite represents a sample of the sea water where the organisms were living.

Simplified History of Carbon Isotopes Across the K/T Boundary

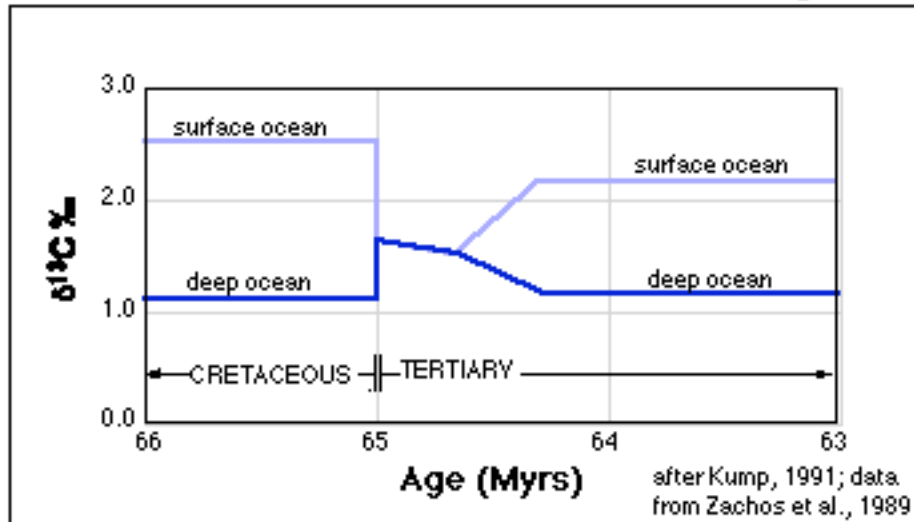


Figure 7.20 Simplified version of changes in the carbon isotopic values of the ocean across the K/T boundary. These measurements come from fossils preserved in deep sea sediments; the record from the surface ocean comes from planktonic organisms, while that of the deep ocean comes from benthonic (bottom-dwelling) organisms.

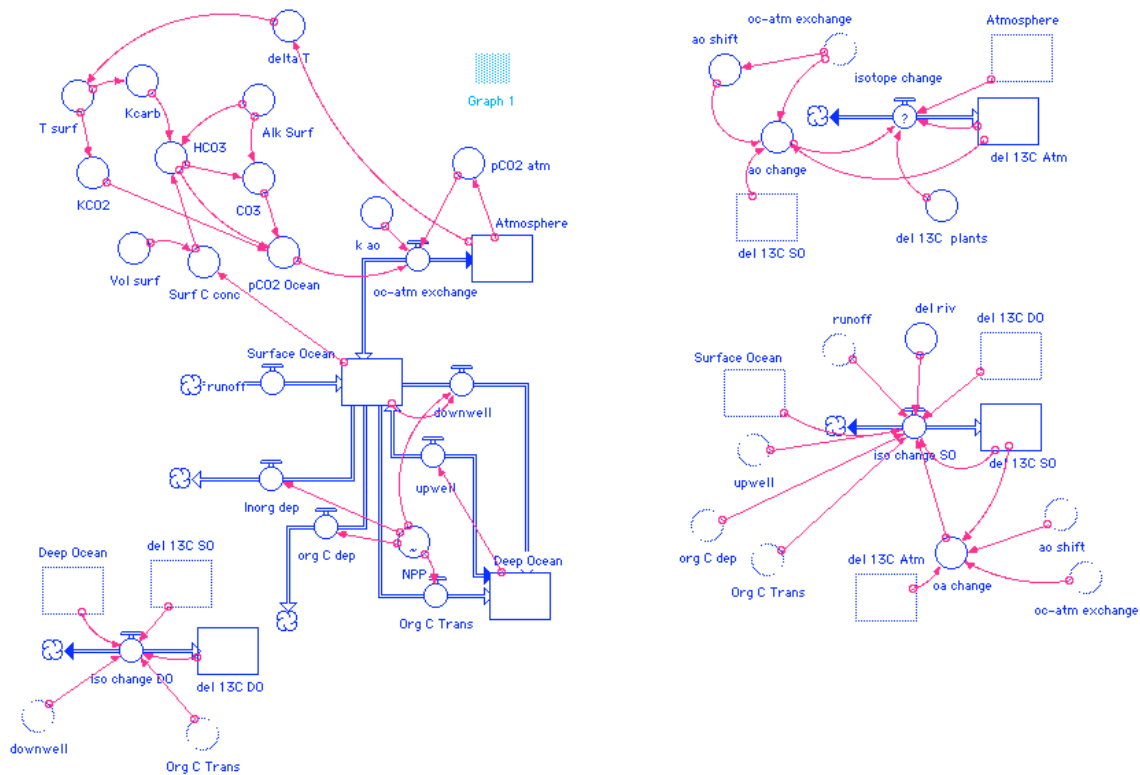
Looking at Figure 7.20, we can see that before the impact, there is the expected difference between the surface ocean and the deep ocean, with the surface having more positive $\delta^{13}\text{C}$ values than the deep ocean because of the operation of the biologic pump. Then, just after the impact, the $\delta^{13}\text{C}$ of the surface water plummets, and the $\delta^{13}\text{C}$ of the deep ocean rises slightly until the two are more or less equal; then begin a slower decline together until about 500 Kyr after the impact, when the two diverge again. The period of time when the surface and deep ocean $\delta^{13}\text{C}$ values are the same represents what is called a "Strangelove" ocean (i.e., the post-apocalyptic ocean) after the Peter Sellers character in Stanley Kubrick's outstanding movie titled Dr. Strangelove. From this isotopic record of what happened, we would like to be able to say something more specific about what happened to the biologic pump. To do this, we need to develop an ocean-atmosphere carbon isotopic model.

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Constructing the Model

This model will be based on the simple ocean - atmosphere carbon cycle model represented in Figure 7.13, with several modifications to help us keep track of the organic carbon and inorganic carbon (carbonate) moving between the surface and deep ocean reservoirs. The reason for doing this is because of a fractionation that occurs when organisms fix carbon from sea water to make their soft parts; this makes the organic carbon much lighter, shifted by -25‰ , while the inorganic carbon will simply be the same as the sea water $\delta^{13}\text{C}$. Figure 7.21 shows the structure of this model, divided up into

different zones; one zone models the mass flows of carbon (in gigatons), while the other zones model the changes in isotopic ratios of the carbon stored in the three different reservoirs.



• **Equations for K/T Ocean-Atmosphere d¹³C Model**

Reservoirs (mass of carbon):

INIT Atmosphere = 600 {Gt C}
 INIT Deep_Ocean = 38000 {Gt C}
 INIT Surface_Ocean = 884.391 {Gt C}

Reservoirs (isotopic ratios of carbon):

INIT del_13C_Atm = -6 {pre-industrial del13C}
 INIT del_13C_SO = 2.5
 INIT del_13C_DO = 1.1

Flows(mass of carbon):

fires = GRAPH(time)
 (0.00, 0.00), (0.5, 0.00), (1.00, 0.00), (1.50, 0.00), (2.00, 0.00), (2.50, 0.00), (3.00, 0.00), (3.50, 0.00), (4.00, 0.00),
 (4.50, 0.00), (5.00, 0.00)
 oc-atm_exchange = k_ao*(pCO2_atm-pCO2_Ocean)
 downwell = ((1*NPP/8)+(140.2/1.4))*(Surface_Ocean/INIT(Surface_Ocean))
 upwell = (150/1.4)*(Deep_Ocean/INIT(Deep_Ocean))
 runoff = 1
 inorg_dep = .6*NPP/8 {carbonate sediment deposited on the sea floor and buried}
 org_C_dep = .4*NPP/8 {organic carbon deposited on the sea floor and buried}
 org_C_Trans = 6*NPP/8 {organic carbon transferred to deep ocean, but not buried}

Flows (isotopic ratios of carbon):

isotope_change = (1/Atmosphere)*((Fires*(del_13C__plants-del_13C_Atm))+ao_change)


```

iso_change_DO = (1/Deep_Ocean)*((downwell*(del_13C_SO-del_13C_DO))+(Org_C_Trans*(del_13C_SO-25-
del_13C_DO)))
iso_change_SO = (1/Surface_Ocean)*((runoff*(del_riv-del_13C_SO))+oa_change+(upwell*(del_13C_DO-
del_13C_SO))+(org_C_dep+Org_C_Trans*25))

```

Converters (masses of carbon):

```

Alk_Surf = 2.24
CO3 = (Alk_Surf-HCO3)/2
HCO3 = (Surf_C_conc-SQRT(Surf_C_conc^2-Alk_Surf*(2*Surf_C_conc-Alk_Surf)*(1-4*Kcarb)))/(1-4*Kcarb)
Kcarb = .000575+.000006*(T_surf-278)
KCO2 = .035+.0019*(T_surf-278)
k_ao = .278 {Gt C/yr/ppm -- the observationally-derived rate constant; this is for the entire surface area of the ocean}
pCO2_atm = Atmosphere*(280/600)
pCO2_Ocean = 350*KCO2*(HCO3^2/CO3)
Surf_C_conc = (Surface_Ocean/12000)/Vol_surf {1e18 moles/m^3}
T_surf = 288 {°K}
Vol_surf = .0363 {units are 1E18 m^3 -- this is the upper 100 m}
NPP = GRAPH(time {Gt C/yr net primary production -- net carbon extracted from sea water by organisms})
(0.0, 8.00), (10.0, 8.00), (20.0, 8.00), (30.0, 8.00), (40.0, 8.00), (50.0, 8.00), (60.0, 8.00), (70.0, 8.00), (80.0, 8.00),
(90.0, 8.00), (100, 8.00)

```

Converters (isotopes of carbon):

```

del_13C__plants = -20 {del13C of fossil fuels}
del_riv = -7.5 {avg isotopic value of carbon delivered by rivers}
ao_shift = if oc--atm_exchange>0 then -2 else -9.5 {the isotopic shift of the ocean-air transfer depends on the direction
of flow -- data from Siegenthaler and Munnich, 1981}
ao_change = if oc--atm_exchange>0 then -oc--atm_exchange*ao_shift else oc--
atm_exchange*(del_13C_SO+ao_shift+del_13C_Atm) {net effect of the ocean-air transfer}
oa_change = if oc--atm_exchange>0 then oc--atm_exchange*(del_13C_Atm+ao_shift-del_13C_SO) else -oc--
atm_exchange*ao_shift {net effect of the ocean-air transfer}

```

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In the carbon mass portion of the model, the flow that was previously called the biologic pump is here broken up into four different flows, which are all fractions of the net primary production, NPP. The NPP here represents all of the carbon, organic and inorganic, fixed by organisms living in the surface oceans. The model is initially set up with an NPP of 8 Gt C/yr; of this, 6.4 Gt is organic carbon, 6 of which is decomposed by microbes and added to the water of the deep ocean, while 0.4 Gt is eventually deposited and buried in sediments on the sea floor. The 1.6 Gt C or carbonate (inorganic carbon) is divided up into 1 Gt (added to the downwelling flow) that gets dissolved on its way into the deep ocean, and 0.6 Gt that is deposited and buried on the sea floor.

The initial reservoir values in this model are intended to approximate the conditions at the end of the Cretaceous, when the Earth was significantly warmer. The atmospheric reservoir was set so that the CO₂ concentration of the atmosphere is three times the present value. The temperature of the surface waters of the oceans was increased by 4°, and then the carbon content was adjusted until the CO₂ concentration matched that of the atmosphere. The isotopic values of the oceanic reservoirs are based on measurements from the shells of organisms, while the isotopic value of the atmosphere, for lack of measured values, is set to the pre-industrial value of -6‰.

The isotopic portion of the model is complicated by the fractionation that occurs when CO₂ is exchanged between the atmosphere and the ocean. If CO₂ moves from the atmosphere to the ocean, there is a -2‰ fractionation, but if it moves the other way, there is a -8‰ fractionation. In the model, this necessitates an "if-then-else" statement.

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Experiments

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1. Sudden, Complete Killing

What happens if we kill off all the organisms in the surface waters, disabling the biologic pump, sending the NPP to 0? More precisely, the questions to ask are: 1) what happens to the carbon cycle as a result of this change?; and 2) how is this change reflected in the carbon isotopes of the ocean reservoirs?. To simulate this sudden, complete killing, change the graph of the NPP so that it is equal to 0 rather than 8 for the duration of the experiment. Make predictions and then run the model for 100 years with time step of 0.1 using the Runge-Kutta 2 method of integration. After studying the short-term effects, run the model out for 2000 years (this will take a few minutes). You may find it helpful to plot the surface and deep ocean $d^{13}C$ values at the same scale, to facilitate comparison with the observed record shown in Figure 7.20.

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2. Varying the Magnitude and Duration of the Kill

In the above experiment, we killed off everything in the oceans (at least as far as the carbon cycle is concerned) and we kept the oceans in this dead state for the duration of the experiment. Comparing the results from experiment with the observed record shows a fairly good agreement, making us think that perhaps the oceans really were effectively dead for quite a long time. But, we might wonder about how severe of a killing is needed to show up as a noticeable change in the isotope record. By "severe" I mean the magnitude of reduction in the biologic pump, and the duration of this reduction. In order to alter the method for defining the severity of the killing or reduction in NPP in the oceans, we will add four new converters to the model, following the scheme described in Figure 7.22.

Scheme for Altering Magnitude and Duration of Killing

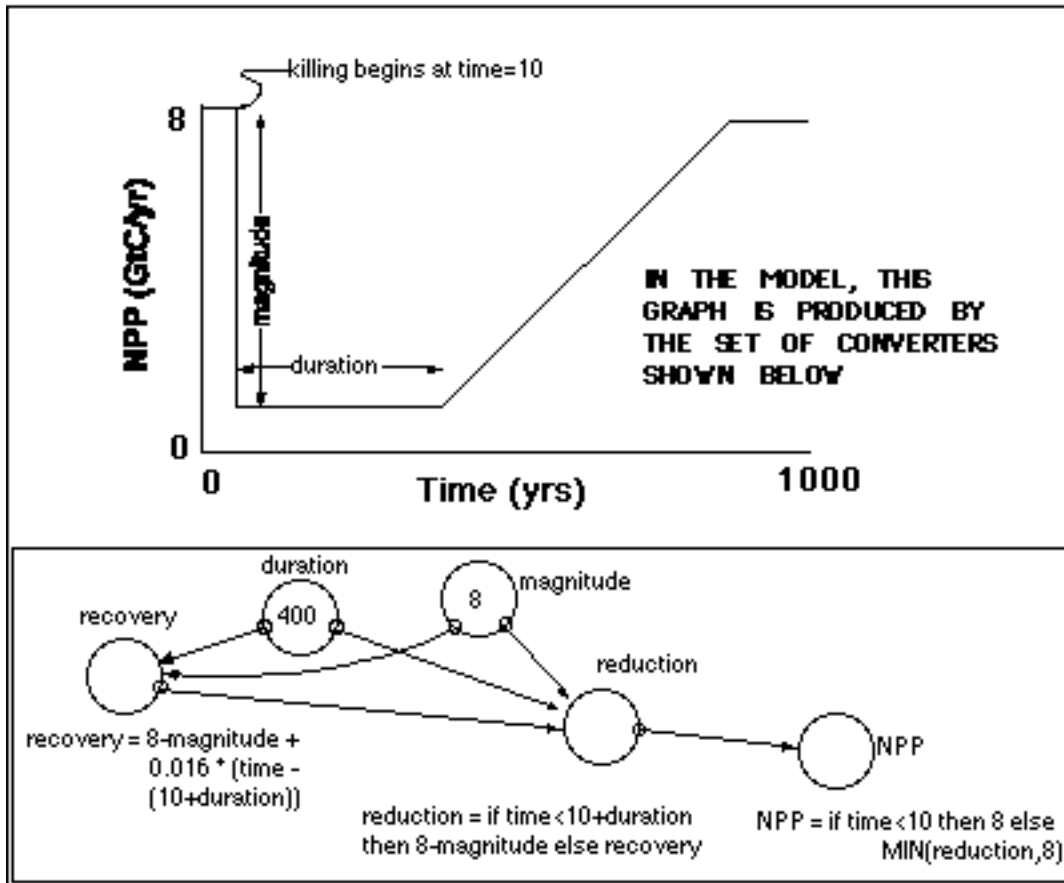


Figure 7.22 Plan for modifying the model in order to investigate the effects of varying the severity of the killing, where severity is defined by the magnitude and duration of the reduction in NPP in the oceans. The equation for recovery is set so that full recovery after complete killing takes place in 500 years (the slope of the recovery is constant).

With this new scheme in place, we can readily change the magnitude and duration of the killing to see how the isotopic values of the ocean reservoirs respond. The primary question to investigate here is what is needed in terms of magnitude and duration to make the surface and deep ocean $d^{13}C$ values equal, as is observed in the post-K/T Strangelove ocean.

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3. Effect of Large-Scale Global Fires

If you recall from the above brief discussion of the soot found in the K/T clay layer, it appears that a significant portion of the land plants burned; this would have released a great deal of light carbon into the atmosphere. What happens to the carbon cycle and especially the carbon isotopes if we include this proposed large-scale burning that took place after the impact (fires ignited by some of the super hot fallout of the impact)? We can represent these fires by modifying the graph that appears inside the Fires flow. On

this graph, which relates the Gt of carbon released by fires over time, we can create a scenario of burning and observe its effects. Let's imagine that the burning is fast and furious beginning at time=10, releasing about 100 Gt/yr, then returning to 0 by time=14. To clearly understand the effect of these fires on the quantities of carbon and the $d^{13}C$ values of the major reservoirs, run this model for about 100 years with no reduction in the NPP. Then, after you have studied the results and understand why the model behaved as it did, combine this same fire-burning scenario with a scenario of complete killing and compare the results with a model in which there are no fires -- this will allow you to see if the fires might have had a significant effect on the $d^{13}C$ values of the oceanic reservoirs in the aftermath of the K/T impact crisis.

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Summary of Carbon Isotope Modeling

In this section, we extended our modeling of the global carbon cycle to investigate the changes in the ratios of carbon isotopes that accompany changes in the distribution of carbon in the global cycle.

The carbon dioxide emitted to the atmosphere by fossil fuel burning has a very different isotopic makeup than the atmospheric reservoir as a whole, thus we can see the human effects on the carbon cycle not only in the increasing amount of carbon in the atmosphere, but also in the changing ratio of carbon isotopes in the atmosphere. The observed record of atmospheric $d^{13}C$ also provides a constraint on the problem of the missing sink -- the problem of where all of the anthropogenic carbon dioxide is going (only 50% stays in the atmosphere).

We also developed a model of the ocean-atmosphere carbon cycle and associated isotopic changes to investigate what happened at the K/T boundary, one of the most important climatic and biotic rises in Earth's history. The model allows us to more clearly interpret the record of carbon isotopic changes in the oceanic realm following the impact. This crisis, which led to the extinction of around 80% of all species appears to have dealt a major blow to the carbon cycle, but the system appears to have recovered nearly completely within about 500,000 years. The climate just after this time appears to have been more or less the same as just before this time. This recovery of the carbon cycle and the climate system as a whole is a remarkable feat and tells us something very important - the whole Earth system is surprisingly resilient on time scales of a million years or so. It has the ability to recover and regenerate its stabilizing mechanisms.

It is important to keep the time scale of recovery in mind when thinking about our present condition and the prospects for our future well-being on this planet. If we do continue to tamper with the climate and the biosphere, it is conceivable that we might cause a crisis that makes the Earth system very inhospitable to us and many other organisms for a very long time relative to our lifetimes, but in the long run, we have every reason to believe that the Earth will recover (with or without our species).

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