Climate change past and present: Carbon cycle analogs

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ABSTRACT

The global carbon cycle plays an important role in the global warming that has become a prevalent and growing concern over the past decade. Anthropogenic carbon emissions perturb the carbon cycle and leave a record of these changes in the isotopic record. These isotopic signatures can be used as an analog to interpret the causes and effects of periods of global warming in the geologic past. This study develops a global carbon model to analyze the effect of different carbon emission scenarios on the carbon cycle as a whole, and on the isotopic signature of pedogenic carbonates specifically. The study shows, based on simulations of four different emission scenarios, that the amount of carbon, the rate of emission, and the time span of emission are all crucial parameters controlling the magnitude of temperature increase, carbon cycle perturbation, and isotopic excursions. Release of 318 Gigatons of carbon over 400 years results in the study’s most extreme changes with temperature increases of 9.3 degrees Celsius, isotope excursions of -7‰ in the pedogenic carbonate record, and overall perturbation of the global carbon cycle. Comparisons to the Paleocene-Eocene Thermal Maximum (PETM) suggest evidence for a combined release of carbon dioxide as well as methane during this period of global warming.

Keywords: global carbon cycle, climate change, global warming, carbon cycle modeling, carbon isotopes, anthropogenic carbon emissions, Paleocene-Eocene Thermal Maximum
INTRODUCTION

Global warming has become a prevalent and growing concern over the past decade. Evidence of shrinking glaciers (Bamber et al., 2007), rising sea levels (Arendt et al., 2002), increasing global surface temperatures (Mann et al., 1998; Pittock, 2005), and larger volumes of carbon found in the atmosphere (Dobson, 2002), has all pointed to rapid global climate change. This global warming has largely been attributed to anthropogenic carbon emitted during the combustion of fossil fuels (Andres et al., 2000; Verdes, 2007) and through the alteration of natural land use caused by soil and forest disruption (Bolin et al., 1979). This massive release of carbon has resulted in the perturbation of the natural global carbon cycle.

Carbon plays an important role in and is seriously affected by climate change processes. Greater concentrations of carbon in the atmosphere as a result of anthropogenic activities results in increased temperatures. The atmosphere plays a role of crucial importance in the global carbon cycle, with even slight disruptions of carbon levels in the atmosphere fundamentally altering other components of the cycle. Because many of these carbon cycle processes function as positive feedbacks causing carbon increases in one reservoir to radiate and multiply in others, warmer temperatures are exacerbated by the increased rates of growth, decomposition, and changing ocean cycles. The carbon cycle also functions as a recorder of climate. The isotopic signature of carbon is altered by many of the cycle’s biological processes. These alterations undergo shifts corresponding to fluctuations in amounts and types of cycling carbon instigated by climatic changes. These isotopic shifts can be stored in the geologic record in a variety
of forms including fossils, sediments, ice cores, and paleosols, and can serve as proxies to be used in reconstructing past climatic events.

While there were no humans in the past modulating climate changes, rapid excursions of atmospheric CO₂ and global temperature do appear in the geologic record. This type of excursion occurred at the boundary of the Paleocene-Eocene about 55 million years ago in an event known as the Paleocene-Eocene Thermal Maximum (PETM). This event was characterized by a global release of isotopically light carbon, and a resulting greenhouse effect that warmed the planet 5-10 degrees Celsius, and is recorded in paleosols and sediments from this period. Use of pedogenic carbonate bearing paleosols has been of particular use to scientists attempting to reconstruct the atmospheric and climactic conditions of the PETM. Several hypotheses have been developed to explain the temperature change, marine and terrestrial isotopic excursions and the mass extinctions that appear in the record of the PETM. Our investigation of a current, anthropogenically instigated, rapid climate change has the potential to inform our study of the PETM. Elements of the changes we see in current carbon cycling, isotope shifts, and global temperatures could potentially help us interpret the nature of causes and effects of climate changes in the past.

This study seeks to investigate the effects of anthropogenically induced rapid climate change on the global carbon cycle, and particularly the pedogenic carbonate isotopic record. The research intends to answer the questions: What effect do anthropogenic emissions have on the carbon cycle? What isotopic signature of anthropogenic fossil fuel CO₂ emissions might we expect the soil carbonate nodule record to show? and What insights might these changes have to offer regarding past
periods of rapid changes in climate and atmospheric CO2 levels? I have developed a model of the global carbon cycle that tracks isotopic signature changes through each reservoir and records the isotopic signature of pedogenic carbonates. First, I run the model in pre-industrial, steady-state conditions at accepted carbon mass and isotope values. The study then utilizes the model to examine the effects of different emission output scenarios on the global carbon cycle. I then compare these results with interpretations of PETM isotopic records.

BACKGROUND

The Carbon Cycle

Carbon is the basic element of life. The global carbon cycle is defined by the movement of carbon atoms through both organic and inorganic reservoirs. This cycle is constrained by, and of essential importance to understanding the mechanisms of the biosphere, providing the processes by which Earth recycles elements (Bolin et al., 1979). These processes operate on time scales that range from days to multimillions of years and transport life creating carbon through the biosphere, lithosphere, hydrosphere, pedosphere, and atmosphere (Kump et al., 2004). The carbon cycle interacts with countless other Earth processes and cycles. It is this complexity and interconnectedness that makes knowledge and understanding of the carbon cycle so important for identifying, predicting, and reacting to the effects of changes to any part of the chain.

Terrestrial Carbon Cycle

The terrestrial carbon cycle is made up of three main reservoirs in addition to the atmosphere, which plays an integral part in each segment of the carbon cycle. Land biota,
litter, and soil form the basis of the terrestrial carbon cycle. The following section describes the processes that transfer carbon between these reservoirs.

**Photosynthesis:**

Photosynthesis is an important component of the carbon cycle, providing a mechanism for transfer from the atmosphere to the land biota. Photosynthesis is defined by the equation

\[ CO_2 + H_2O \rightarrow CH_2O + O_2 \]

in which carbon dioxide and water are transformed into carbohydrates and oxygen gas (Kump et al., 2004), forming the basis of gross primary productivity, or the rate at which energy is stored as organics that can be used as food materials (Odum, 1971).

Chloroplasts in leaves contain chlorophyll, which absorbs light with wavelengths between 400 and 700 nm, splitting a water molecule into hydrogen and oxygen creating energy to generate carbohydrates (Smil, 1985).

Photosynthesis is limited by a number of environmental parameters. The availability of water and nutrients alters the rate of primary productivity. In the process of taking up carbon dioxide, plants lose substantial amounts of water vapor (Good and Bell, 1980), thus, in times of droughts plants will close their stomatal openings to conserve water, decreasing the amount of CO₂ uptake (Goudriaan and Ajtay, 1979). Though the role of nutrients is poorly understood due to their complex interactions with atmospheric gases, it is generally concluded that access to nitrogen and phosphorous is also critical to the photosynthetic process (Gifford et al., 2000). Increases in atmospheric CO₂ can lead to increases in plant productivity through a process known as the CO₂ fertilization effect. When atmospheric CO₂ concentrations increase, leaves that are filled
with CO2 decrease the conductance of their stomata, taking in less carbon and losing less water, increasing water use efficiency of the plant (Royer et al., 2001). This trend is subject to an upper limit at which the plant becomes saturated in CO2 and does not intake additional amounts (Goudriaan and Ajtay, 1979). The effect of temperature on photosynthesis is not entirely clear. Increases in temperature generally lead to increases in metabolic processes, and theoretical models suggest that plant growth should do the same (Gifford, 1992; Woodward and Smith, 2000). However, the strong correlation between temperature and other rate limiting parameters and the corresponding increase in plant respiration (Piao et al., 2008) that accompanies temperature change tend to obscure the magnitude of this positive relationship.

The equation for photosynthesis in the model must correspond to these conditions, showing an increased rate in relation to temperature and CO2 concentration increases to a certain point. The initial global flow of carbon in this pathway, based on experimentation and observation, should be approximately 100 Gigatons of carbon per year (GtC/yr) (Bice, 1997; Siegenthaler and Sarmiento, 1993). The resulting equation that satisfies these conditions is

\[ F_p = \left( \frac{P_{\text{max}} \times pCO_{\text{2Eff}}}{Khs + pCO_{\text{2Eff}}} \right) \times \left( 1 + \left( T_{\text{sens}, p} \times \text{GlobalTemp}\Delta \right) \right) \]

Where

\[ F_p = \text{the global rate of CO2 uptake by photosynthesis, measured in Gt/yr} \]

\[ P_{\text{max}} = \frac{(Khs + (pCO_{\text{2atm,initial}} - pCO_{\text{2atm,min}})) \times F_{p,\text{initial}}}{(pCO_{\text{2atm,initial}} - pCO_{\text{2atm,min}})} \]

And forces the equation to give the proper starting value
\( K_{hs} = 62.5 \) parts per million (ppm), this is the half-saturation value, the atmospheric CO\(_2\) concentration at which the rate of photosynthesis is half of the ultimate saturation value, given the temperature

\( pCO_{2_{atm,initial}} = 280 \) ppm, this is the pre-industrial atmospheric CO\(_2\) concentration

\( pCO_{2_{atm,min}} = 30 \) ppm, this is the atmospheric CO\(_2\) concentration below which no photosynthesis can occur

\( F_{p,initial} = 100 \) Gt/yr, this is the initial pre-industrial value for global photosynthesis

\( Tsens_p = 0.04 \), this is the temperature sensitivity of photosynthesis, and indicates in the increase in \( F_p \) per one Celsius degree of warming

\[ GlobalTemp\Delta = (pCO_{2_{atm}} - 280) * 0.01 \]

**Plant Respiration**

Plant respiration makes up the other component of gross primary production, transferring carbon from the land biota to the atmosphere, and is defined by the equation (Kump et al., 2004)

\[ CH_2O + O_2 \rightarrow CO_2 + H_2O \]

The process of respiration occurs as both photorespiration and dark respiration, using stored energy created during photosynthesis to synthesize new structures and to maintain biological functions (Gifford and Jenkins, 1982). Net primary production refers to the amount of respiration subtracted from the total amount of photosynthesis. The ratio of photosynthesis to respiration as a global average is approximately 2:1 (Kump et al., 2004).

Environmental parameters play a relatively small role in the regulation of respiration rates (Rees, 1994). Species and age differences account for much of the
variance in global respiration rates. Empirical research points to both slightly increased and decreased rates of respiration at elevated CO₂ concentrations with no clear trends (Gifford et al., 2000; Norby et al., 1996) and different reactions of respiration to increased CO₂ in the short and long term (Gifford, 2003). Changes in carbon concentrations or temperature that result in increased plant growth will lead to a corresponding increase in respiration (Beevers, 1961). However, this increased respiration is an effect of altered photosynthetic rates, and is not independently responsive to climatic or carbon concentration changes (Rees, 1994).

In the model, the rate of plant respiration has been generalized, and is given by the equation in which the non-temperature sensitivity of plant respiration and the 2:1 ratio of photosynthetic production to respiration are taken into consideration (Bice, 1997; Kwon and Schnoor, 1994).

\[ F_{PR} = F_p \times \frac{50}{100} \]

\( F_{PR} \) = the rate of global plant respiration in GtC/yr

**Litter Fall and Litter Respiration**

Processes enacted by litter fall transfer carbon from the land biota reservoir to the atmosphere and soil reservoirs. Organic material enters soil directly or indirectly through photosynthesis. Leaves and other organic matter fall onto the soil surface in the form of litter, or are contributed below ground through plant roots (Ugolini and Spaltenstein, 1992). If the land biota is in steady state, the amount of total (above and below ground) litter fall is equal to the difference between photosynthetic output and respiration. Once plant material is deposited, it decomposes. Material that decomposes on the surface of the soil respires CO₂ directly to the atmosphere through litter respiration. Organic matter
that enters below ground or undergoes burial before decomposition releases CO₂ into the soil atmosphere, and does not contribute to litter respiration (Schlesinger et al., 2000).

Litter fall responds to increases in temperature and carbon concentrations as a function of plant responses to such changes. Increased plant productivity as a result of CO₂ fertilization increases the abundance of carbon available for transfer in the form of litter. Warmer temperatures also increase the activity of the microbial communities that contribute CO₂ to litter respiration (Ajtay et al., 1979).

Litter fall is represented in the model as a proportion of the land biota reservoir by the equation (Bice, 1997; Siegenthaler and Sarmiento, 1993)

\[ F_{LF} = \frac{LandBiota}{Initial} \times \frac{25}{LandBiota} \]

\[ F_{LF} \] is the rate of global litter fall in GtC/yr

Litter respiration and burial rates are given by the following equations which take into account the amount of litter fall and the temperature sensitivity of the microbial communities that facilitate respiration (Bice, 1997; Siegenthaler and Sarmiento, 1993).

\[ F_{LR} = \frac{Litter}{Initial} \times \left( \frac{21}{Litter} \right) \times \left( 1 + \left( Tsens_{SR} \times \frac{GlobalTemp\Delta}{21} \right) \right) \]

\[ F_{LR} \] is the rate of global litter respiration in GtC/yr

\[ Tsens_{SR} = 0.1 \] (Gifford, 1992)

\[ F_{B} = \frac{Litter}{3.4} \times \frac{80}{\text{GtC/yr}} \]

\[ F_{B} \] is the rate of global burial in GtC/yr

**Soil Respiration**

The organic materials that are not decomposed and respired by litter respiration enter the soil. These organic materials, entering the soil via roots and burial of litter fall, undergo decomposition by microbes and are released into the atmosphere in the form of
CO$_2$ in a process known as soil respiration (Kwon and Schnoor, 1994). Much of this material is found near the surface of the soil reservoir, in which case it is subject to microbial decay, and is respired within one to three years (Schlesinger et al., 2000). Through processes of soil mixing a small percentage of organic matter, about 5% of the total organic soil carbon reservoir, is buried and does not undergo decomposition (Wardle, 1992). Other forms of soil carbon include charcoal (Schlesinger et al., 2000), elemental carbon and pedogenic carbonates, which will be discussed in more detail later. Most of the carbon stored in the soil reservoir is in the form of humus, a metabolic byproduct of microbial decomposition including humic acid, CO$_2$ and H$_2$O, that provides water and nutrient holding capabilities to soils (Reiners et al., 1972; Schlesinger et al., 2000). Humus is the most chemically active component of the soil reservoir due to the variety of chemical forms it takes, its large surface area, and high charge densities (Van Pelt and Zobeck, 2001). Humus has been radiocarbon dated on the scale of hundreds to thousands of years (Campbell et al., 1967) and represents the portion of the soil carbon reservoir with the slowest turnover.

Accumulation of soil organic matter is dependent on moisture and temperature. In cold climates, for example, the rate of net primary production exceeds soil decomposition, resulting in a buildup of organics in the soil until temperatures rise and decomposition is stimulated. Generally, an ambient temperature of 25°C will result in a balance between production and decomposition (Ajtay et al., 1979). An increase in temperature can trigger more rapid and continuous microbial activity, resulting in an increased rate of soil respiration, decreasing the amount of soil organic matter. This decrease can potentially free up nitrogen and other important nutrients to aid in increased
net primary productivity, triggering a positive feedback cycle and greater amounts of soil respiration (Harvey, 2000). Warming can also have the effect of increasing soil carbon storage over time, such as that seen after the ice age of 10,000 years ago in the form of tundra and boreal forests (Harrison and Bonani, 2000), though this relationship is less well constrained for the modern environment (Schlesinger et al., 2000). Increases in soil moisture will also act as a catalyst for increased microbial activity. In the model soil respiration is given by the following equation (Bice, 1997; Siegenthaler and Sarmiento, 1993)

\[ F_{sr} = SoilDisruption + (28.4 / Soil _ Initial) * Soil * (1 + (T_{sens} _ sr * GlobalTemp\Delta)) \]

\[ F_{sr} = \text{the rate of global soil respiration in GtC/yr} \]

\[ SoilDisruption = \text{an input defined graphically in the model, initial value is zero when the model is in steady state} \]

**Runoff**

Runoff transfers carbon from the terrestrial carbon cycle to the ocean – atmosphere portion of the global carbon cycle. A very small portion of soil carbon that is not respired is transported by wind, rivers, and streams to eventually reach the ocean (Sarmiento and Sundquist, 1992). The erosion that generates this transportable carbon ranges from entirely weathering limited to entirely transport limited (Stallard and Edmond, 1987). Weathering limited erosion occurs when the weathering reactions in the soil create less material than could potentially be removed by transport. Transport limited erosion represents the opposite end of the erosion continuum in which the rate of eroded material production exceeds the rate at which transport can remove the material (Stallard, 1992). These eroded substances run off in overland flow (across the surface),
interflow (in the upper layer of the soil cover), or subsurface runoff by groundwater eventually depositing carbon that has undergone very different soil residence times, into the ocean (Kempe, 1979a). When runoff carbon enters the ocean, it has been oxidized from organic carbon to inorganic carbon (Kwon and Schnoor, 1994).

Runoff is constrained by the properties of the soil which creates it, and therefore responds to changes in temperature, CO2 concentrations and moisture as a function of changes within the soil reservoir. Runoff is also particularly sensitive to the effects of agriculture, and increases significantly with the loss of usual vegetation cover (Schlesinger, 1986), though the complexity of this sensitivity excludes it from the model.

In the model, runoff constitutes a small flow defined by the equations (Bice, 1997; Siegenthaler and Sarmiento, 1993)

\[ F_{R1} = \text{Litter} \times \left( \frac{0.2}{\text{Litter}_{\text{Initial}}} \right) \]

\[ F_{R2} = \text{Litter} \times \left( \frac{0.4}{\text{Litter}_{\text{Initial}}} \right) \]

which separate runoff that enters the warm surface ocean (\( F_{R1} \)) constituting approximately 2/3 of the global oceans, and the cold surface ocean (\( F_{R2} \)) making up the other 1/3 (Kwon and Schnoor, 1994). These reservoirs are separated in the model due to their distinct relationships to the processes of the carbon cycle.

**Oceanic Carbon Cycle**

The oceanic carbon cycle is made up of three main reservoirs in addition to the atmosphere. The deep ocean, warm surface ocean, and cold surface ocean soil form the basis of the oceanic carbon cycle. The following section describes the processes that transfer carbon between these reservoirs.

*Ocean-Atmosphere Exchange*
CO₂ is transferred continuously between the ocean and the atmosphere. This exchange plays an important role in the global carbon cycle due to the size of the oceanic carbon reservoir which contains more than 50 times as much carbon as the atmosphere (Druffel et al., 1992). This transfer process, therefore, has the potential to absorb or release large quantities of carbon. The ocean atmosphere exchange is driven by differences in the CO₂ concentrations of the air and ocean surface water. In areas of high primary productivity, where CO₂ is caught up in biological processes, CO₂ diffuses from the more highly concentrated atmosphere reservoir into the ocean. In areas of upwelling, the surface water has a high concentration of CO₂ from deep ocean transfer, and diffuses CO₂ to the atmosphere until the partial pressures are equal (Freyer, 1979; IPCC, 2001). This diffusion is also limited by a thin film of surface water that does not mix as a result of wind or currents (Broecker et al., 1979). Diffusion across this layer has been defined through experiment as a somewhat poorly constrained gas transfer coefficient (Wanninkhof and McGillis, 1999).

The ability of seawater to exchange CO₂ with the atmosphere is also controlled by temperature and the chemistry of the water. The solubility of CO₂ is temperature dependent. CO₂ is outgassed by warmer waters and taken up from the atmosphere by cooler waters (Broecker and Peng, 1992). This solubility ultimately affects the equilibrium processes described below. Carbon exists in the ocean in several forms. The largest amount of carbon occurs as dissolved inorganic carbon in the forms CO₂, HCO₃⁻, and CO₃²⁻ (Siegenthaler and Sarmiento, 1993). The interaction of these three species is complex and controlled by a number of parameters.
When CO₂ is dissolved in water, carbonic acid is formed as described in the equilibrium equation

\[ CO_2 + H_2O \leftrightarrow H_2CO_3 \]

The disassociation of this acid into carbon anions and hydrogen cations determines the pH of the seawater (Kump et al., 2004). The first step in disassociation releases one hydrogen atom which forms bicarbonate

\[ H_2CO_3 \leftrightarrow H^+ + HCO_3^- \]

As disassociation proceeds, and the number of H⁺ ions increases, this equilibrium equation would reverse, going to the left, to create more carbonic acid in maintenance of equilibrium. Further disassociation of a bicarbonate ion results in a carbonate ion as shown in the equilibrium equation

\[ HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \]

In this manner bicarbonate and carbonate ions are kept in equilibrium for a given concentration of H⁺ ions (Kump et al., 2004).

The alkalinity of the ocean is also a parameter controlling the relative concentrations of carbon dioxide, bicarbonate, and carbonate. Alkalinity of the ocean can be described by the equation

\[ \text{Alkalinity} = [HCO_3^-] + 2[CO_3^{2-}] \]

and functions as a measure of the excess positive ions in the water that the negative charges of bicarbonate and carbonate will balance to achieve equilibrium (Bice, 1997). More excess positive charge will result in greater amounts of carbon occurring as carbonate, since it carries a negative 2 charge, less excess positive charge will alternately result in more bicarbonate. Thus, the concentration of total dissolved inorganic carbon
and alkalinity can be used to determine the ratio of $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$. This can be related to the concentration of CO$_2$ through the equation

$$p\text{CO}_2 = K\text{CO}_2 \left( \frac{[\text{HCO}_3^-]^2}{[\text{CO}_3^-]} \right)$$

in which $K\text{CO}_2$ is a combination of equilibrium constants for CO$_2$, CO$_3$, and HCO$_3$ (Bice, 1997; Walker, 1991). The following equations describe the ocean-atmosphere transfers for the cold and warm surface ocean reservoirs (Bice, 1997; Broecker and Peng, 1993; Kwon and Schnoor, 1994; Walker, 1991)

$$\text{Atm} - \text{CSO Transfer} = \text{AreaCO} \times K\text{CO} \times (p\text{CO}_2_{\text{am}} - p\text{CO}_2_{\text{CO}})$$

$\text{Atm} - \text{CSO Transfer}$ = the global rate of carbon transfer between the cold surface ocean and the atmosphere in GtC/yr

$\text{AreaCO} = 1/3$

$K\text{CO} = \text{is the gas transfer coefficient of 0.278 GtC/ppm/yr}$

$$\text{Atm} - \text{WSO Transfer} = \text{AreaWO} \times K\text{WO} \times (p\text{CO}_2_{\text{am}} - p\text{CO}_2_{\text{WO}})$$

$\text{Atm} - \text{WSO Transfer}$ = the global rate of carbon transfer between the warm surface ocean and the atmosphere in GtC/yr

$\text{AreaWO} = 2/3$

$K\text{WO} = K\text{CO}$

**Advection**

Advection is the process by which carbon is transferred through surface currents from the warm surface ocean to the cold surface ocean (Kwon and Schnoor, 1994). The complex interaction of surface wind patterns and ocean currents create large scale circular circulation patterns known as gyres that force the exchange of water and carbon
through the world’s oceans (Kump et al., 2004). Ocean waters near the equator are heated by solar radiation then circulated toward the polar oceans where it cools. This cold surface ocean water is eventually circulated back toward the equatorial oceans. This cycling provides a necessary global exchange of solar energy. The transfer of carbon from the warm ocean to the cold ocean is greater than the carbon transferred in the reverse process, due to the sinking of cold waters to the deep ocean reservoir (Fung and Takahashi, 2000; Siegenthaler and Sarmiento, 1993).

The exact relationship between advection and the parameters that constrain it is not entirely understood. Increases in temperature and CO₂ concentrations are likely to change the overall structure of the currents as waters become warmer and transport different amounts and forms of carbon. The model therefore operates with a simplified version of advection that depends only on the volume of the cold ocean (Bice, 1997; Kwon and Schnoor, 1994).

\[
F_{ADV} = 20 \times \left( \frac{\text{WarmSurfOcean}}{\text{WarmSurfOcean Initial}} \right)
\]

\(F_{ADV}\) = the global rate of advective flows in GtC/yr

**Marine Biota Exchange**

The marine biota exchange facilitates carbon transfer from both the cold and warm surface oceans to the deep ocean, and also interacts with the atmosphere-ocean exchange. Photosynthetic organisms live primarily in the photic zone of the ocean, and provide the basis of the marine food chain and organic carbon cycle (Caldeira et al., 2000). These organisms use upwelling nutrients and dissolved CO₂ from the surrounding waters to photosynthesize, and respire CO₂ back into these surface waters. Some of the organic matter produced is consumed by microorganisms and small invertebrates,
referred to collectively as zooplankton. These zooplankton in turn create carbon rich fecal pellets which, along with decaying organic matter, the equivalent of marine litter, fall through the water column (Kump et al., 2004). The majority of this material is oxidized to inorganic carbon during its passage through the water column or recycled by anaerobic decomposers on the sea floor, with only about 0.1% of the organic material reaching the ocean floor to be buried as marine sediment (Kump, 1991). Organic material on its passage through the ocean is also consumed and decomposed by marine animals and microbes, remineralized and released back into the water as CO₂ (Murray, 1992). Carbon is also taken out of the surface waters by marine organisms to be incorporated into carbonate shells. The shells and soft bodies of these organisms follow the path of other organic material through the water column. A small fraction of the CaCO₃ is deposited on the sea floor above the compensation depth (Bolin et al., 1979). These processes of photosynthesis, settling organics and shells, and decomposition collectively result in the biological pump which transfers CO₂ and nutrients from the surface ocean to the deep ocean reservoirs (Kwon and Schnoor, 1994).

The biological pump is thought to be limited primarily by the availability of nutrients. In empirical studies phosphorous and nitrogen have been shown to significantly influence the rates of biological activity in the warm surface oceans (Murray, 1992). Iron appears to be the limiting factor in cold ocean environments (Martin and Fitzwater, 1988). Increases in both temperature and atmospheric CO₂ concentrations could disrupt oceanic circulation, as described below. The disruption of temperature dependent vertical water transport would reduce the cycling of nutrients from the deep ocean to the surface ocean reservoir. Decreased marine biological activity would result
in higher levels of inorganic carbon and partial pressures of CO₂ near the surface, altering the ocean atmosphere exchange. Reduced vertical mixing would also decrease the amount of inorganic carbon transferred from the deep ocean to the surface, complicating the outcomes of possible temperature increase predictions (IPCC, 1994).

In the model the biological pump of carbon from the warm and cold surface ocean are assumed to be constant (Bice, 1997).

\[ F_{WOBP} = 6 \]

\[ F_{COBP} = 4 \]

\( F_{WOBP} \) = global rate of carbon flow from warm ocean biological pump in GtC/yr

\( F_{COBP} \) = global rate of carbon flow from cold ocean biological pump in GtC/yr

**Sedimentation**

The portion of organic and inorganic carbon from the biological pump that is not respired or decomposed and reaches the ocean floor above the calcite compensation depth is deposited as sediment (Bolin et al., 1979). Over thousands of years, these sediments are buried, and given the proper environmental conditions, are lithified to form sedimentary rocks (Kump et al., 2004). When these rocks are subducted they transport carbon back into the Earth where it will eventually reenter the surface carbon cycle through tectonic activity.

The sedimentation rate is dependent on the rate of oceanic primary production (De Vooys, 1979). However, because of its small size and the complexity of the processes determining sedimentation rates it is represented as a constant of 0.6 GtC/yr in the model (Bice, 2008).

**Tectonic Activity**
Volcanic eruptions also contribute carbon to the atmosphere (Gerlach, 1991). CO₂ deposited through sedimentation in the deep ocean is recycled through the rock cycle and emitted by either metamorphic or volcanic activity in to the atmosphere (Kempe, 1979a). The net carbon transfer per year through volcanism is relatively small, and varies with the number and magnitude of eruptions. In the model this flow is represented as an average value of 0.6 Gt C/yr (Bice, 1997).

**Downwelling**

The inequality in the advective exchanges of carbon between the cold and warm surface oceans is made up through the process of downwelling, which transports carbon from the surface to the deep ocean (Siegenthaler and Sarmiento, 1993). Ocean water converges in the middle of the gyres due to the surface ocean currents described above, the Earth’s rotation, and the friction of layers of ocean water sliding past one another. This convergence creates a unstable build up of water, which eventually sinks (Kump et al., 2004). Downwelling occurs near the poles in the cold surface ocean compartment (Kwon and Schnoor, 1994). The low temperatures resulting from surface cooling and high salinity of this water due to the formation of sea ice, yield high densities that contribute to the downward movement of the water carrying carbon to the deep ocean reservoir at depths of 100-1000 meters (Bolin et al., 1979). Downwelling plays an important role in ocean circulation by entirely mixing the ocean waters over the course of a thousand years (Kempe, 1979b).

The amount of carbon transported through downwelling waters is a function of how much carbon is stored in the cold surface ocean reservoir, and is therefore subject to changes in temperature and CO₂ concentrations within the ocean and the atmosphere.
CO\textsubscript{2} is more soluble in cold water than warm water, thus as water temperatures increase, the amount of CO\textsubscript{2} able to be stored in the ocean decreases (Caldeira et al., 2000). Simulations of ocean currents under changing temperature regimes have shown significant reduction of this downward circulation when surface waters are warmer, decreasing the temperature and salinity differences that make downwelling possible (Manabe and Stouffer, 1993). Though the amount of downwelling as a percentage of cold surface water can vary from year to year (Bjorkstrom, 1979) the equation used in the model assumes a constant ratio, and defines the rate of downwelling as (Bice, 2008; Walker, 1991)

\[ F_{DW} = \text{ColdSurfOcean} \times \left( \frac{90.2}{\text{ColdSurfOcean - Initial}} \right) \]

\[ F_{DW} = \text{Global rate of carbon flow through downwelling in GtC/yr} \]

**Upwelling**

Downwelling transports more carbon than is required to balance the inequalities in the advective exchanges. Upwelling is the converse process that moves this excess sink of carbon from the deep ocean reservoir to the warm surface ocean. In areas of surface water divergence, particularly around continental edges and near the equator, cool deeper waters rise up to fill in the thinned warm surface layer (Kump et al., 2004). Upwelling, in addition to mixing waters, provides an important flux of nutrients within the ocean. This nutrient rich flow of upwelling contains more carbon than downwelling due to the transfer of carbon to the deep ocean reservoir through the biological pump (Kwon and Schnoor, 1994).

The amount of carbon transported through upwelling is a function of the amount of carbon stored in the deep ocean reservoir. Increased temperatures and CO\textsubscript{2}
concentrations affect upwelling processes in much the same way as downwelling processes. In the model upwelling is represented by the equation (Bice, 2008)

\[ F_{UW} = 99.6 \left( \frac{DeepOcean}{DeepOcean_{Initial}} \right) \]

\[ F_{UW} = \text{Global rate of carbon flow through upwelling} \]

**Human Processes in the Carbon Cycle**

**Fossil Fuel Burning**

Anthropogenic burning of fossil fuels has perturbed the natural carbon cycle and resulted in a net increase in the CO\(_2\) concentration of the atmosphere (Andres et al., 2000). The combustion reaction for natural gas is

\[ CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \]

Reactions for oil and coal, the other main components of fossil fuel burning also transform fossilized organic material using oxygen into water and carbon dioxide which is then released to the atmosphere (Kump et al., 2004). The use of fossil fuels began during the Industrial Revolution, and is currently releasing approximately 6 GtC/yr. This additional carbon dioxide remains in the carbon cycle for long periods of time, altering all reservoirs and processes, resulting in the compounding effect of continued emissions (Kasting, 1998). Fossil fuel burning will be initially ignored in the model in order to achieve steady state, and later added as a graphical function.

**Land Use Changes**

The land biota, litter, and soil reservoirs of the carbon cycle have all undergone considerable changes as a result of human activities. Agriculture and development have resulted in deforestation and soil disturbances (Broecker et al., 1979). Biomass that is cut
down releases carbon to the atmosphere as it is burned or decays. The effect of this additional carbon input to the atmosphere is exacerbated by the corresponding shrinkage of the land biota reservoir (Kump et al., 2004). This carbon release was greater than the release from fossil fuels until about 1960, and in 1980 was between 22 and 43 percent of the total carbon released through fossil fuels (Woodwell et al., 1983). Agriculture causes disturbance of the soil through tilling, and increases the rate of microbial decomposition and soil respiration fundamentally altering the carbon storage capabilities of the soil, and releasing excess soil to the atmosphere (Houghton, 2000; Woodwell et al., 1983). Land use changes will also be initially ignored in the model and put in after steady state has been reached.

**Carbon Isotopes**

There are three naturally occurring carbon isotopes. Most carbon occurs as $^{12}\text{C}$, with about 1% occurring as $^{13}\text{C}$ and 1E-10% occurring as $^{14}\text{C}$. Both $^{12}\text{C}$ and $^{13}\text{C}$ are stable isotopes (Bice, 1997). Therefore, the ratio of $^{12}\text{C}$ to $^{13}\text{C}$ can be used as a record of changes in the carbon cycle and its processes. Fossils, sediments (Rogers, 1993), and pedogenic carbonates (Cerling and Quade, 1993), among other things, all record the $\delta^{13}\text{C}$ value of the isotopic conditions under which they were formed, and can be used to determine the origin and history of these materials. Most importantly for our study is the ability to reconstruct paleotemperature and paleoclimate from these isotope records, and the use of carbon isotopes in constraining fluxes in and out of each carbon reservoir (Ciais et al., 1995; Sharp, 2007).

Isotopic ratios are given by the standard equation (Ehleringer et al., 2000b)
\[ \delta^{13}C = \left( \frac{^{13}C}{^{12}C} \right)_{\text{Sample}} - \left( \frac{^{13}C}{^{12}C} \right)_{\text{Standard}} \right] \times 1000 \]

in which the standard is taken from Pee Dee Belemnites, and results in a per mil ratio (Sharp, 2007). Different reservoirs in the carbon cycle naturally have differing carbon isotope ratios, determined by the biological activity occurring within them, as well as the amounts and isotopic ratios of carbon flowing in and out of them. Some processes fractionate isotopes, which leads to a change in the ratio of carbon. Fractionation occurs when certain processes preferentially choose one form of carbon over another.

Photosynthetic organisms, for example, favor \(^{12}\text{C}\) to incorporate into their tissues, and thus shift the isotopic signature of the carbon they incorporate by approximately negative 20‰ (Ehleringer et al., 2000b; Sharp, 2007). This shift alters both the atmospheric reservoir out of which carbon used in photosynthesis flows as well as the isotopic composition of the land biota reservoir into which this fractionated carbon flows.

Isotopic shifts play a particularly important role in the discussion of the effect of fossil fuel emissions on the carbon cycle. Fossil fuel burning releases isotopically light carbon into the atmosphere. Fossil fuel emissions have \(\delta^{13}\text{C}\) values between -20 and -30 because they were created from organic materials which preferentially incorporated \(\delta^{12}\text{C}\) into their tissues (Andres et al., 2000). The massive anthropogenic release of this isotopically light carbon will allow us to trace isotopic changes in the carbon cycle, as well as changes in reservoir masses of carbon.
In the model carbon isotopes have been recorded for each reservoir. The changes in $\delta^{13}C$ values were calculated using the following basic equation modified from (Bice, 2008; Walker, 1991).

$$\Delta \delta^{13}C_{\text{RESERVOIR}} = \left( \frac{1}{\text{Reservoir}} \right) \ast \left( (F_I \ast (\delta_I - \delta_R)) + (F_{I2} \ast (\delta_{I2} - \delta_R)) - (F_O \ast (\delta_O - \delta_R)) \right)$$

$F_I, F_{I2} =$ A flow of carbon into the reservoir

$\delta_I = \delta^{13}C$ value of the inflow

$\delta_R = \delta^{13}C$ value of the reservoir in question

$F_O =$ A flow of carbon out of the reservoir

$\delta_O = \delta^{13}C$ value of the outflow

This equation is expanded to include as many inflows and outflows as are present for each reservoir. The $\delta^{13}C$ value of each inflow is given by the $\delta^{13}C$ value of the reservoir if flows out of to arrive at the reservoir of interest. The $\delta^{13}C$ of each outflow is the same as the $\delta^{13}C$ value of the reservoir. If a flow out of a reservoir fractionates isotopes, the value of this fractionation ($Frac$) is included in the equation as a separate term

$$\Delta \delta^{13}C_{\text{RESERVOIR}} = \left( \frac{1}{\text{Reservoir}} \right) \ast \left( (F_I \ast (\delta_I - \delta_R)) + (F_{I2} \ast (\delta_{I2} - \delta_R)) - (F_O \ast ((\delta_O - Frac) - \delta_R)) \right)$$

as is the fractionation value of an flow into a reservoir

$$\Delta \delta^{13}C_{\text{RESERVOIR}} = \left( \frac{1}{\text{Reservoir}} \right) \ast \left( (\delta_I - Frac) - \delta_R \right) + (F_{I2} \ast (\delta_{I2} - \delta_R)) - (F_O \ast (\delta_O - \delta_R)) \right)$$

**Pedogenic Carbonates**

Pedogenic carbonates are carbonates precipitated within upper soil horizons. These carbonates form under arid to sub-humid climates in dry soils where precipitation
is generally less than 100 cm/year (Bowen and Beerling, 2004). More rainfall removes calcium ions from the soils preventing the formation of pedogenic carbonates. The calcium that forms these carbonates is typically derived from dust and Ca$^{2+}$ dissolved in precipitation (Royer et al., 2001), while the carbonate ion comes from the atmosphere and biological processes such as decomposition and root respiration (Cerling et al., 1989). The isotopic composition of pedogenic carbonates is controlled by the isotopic composition of CO$_2$ released through soil respiration, soil temperature and porosity, the rate of soil CO$_2$ production, (Cerling, 1991a; Cerling and Quade, 1993), and the ratio of C$_3$ to C$_4$ plants in the ecosystem (Cerling, 1991b; Cerling et al., 1989). The isotopic composition of atmospheric CO$_2$ is also a parameter that controls the $\delta^{13}$C of pedogenic carbonates due to atmospheric mixing and diffusion is soils (Cerling, 1991a). Because soil respired CO$_2$, atmospheric CO$_2$, C$_3$, and C$_4$ plants all have different isotopic signatures of approximately -26, -6.5, -27, and -13 respectively (Cerling et al., 1989), it is possible to track the relative contributions of CO$_2$ from each source to a pedogenic carbonate based on its $\delta^{13}$C value.

This tracking capability has important implications for the reconstruction of paleoclimate through analysis of paleosols containing pedogenic carbonates, especially for periods of geologic history for which other proxies for paleoatmosphere do not exist (Cerling, 1991a). The $\delta^{13}$C of CO$_2$ is approximately constant below an attenuation depth of 30cm, thus carbonates formed below this depth, that have not undergone overprinting or diagenesis give reliable estimates of the partial pressure of CO$_2$ in the atmosphere at the time of formation (Cerling, 1984; Cerling, 1992). High levels of atmospheric CO$_2$ during periods in geologic history would result in significant additions to soil CO$_2$ and
studies have shown the resulting shift in the isotopic signature of the soil carbonates precipitated during this period (Cerling, 1991a).

Instead of using the isotopic signatures of pedogenic carbonates to determine atmospheric pCO₂, the model will use atmospheric pCO₂ output to calculate the $\delta^{13}C$ value of pedogenic carbonates. These values can then be compared to those found during periods of rapid climate change in geologic history. In the model the isotopic signature of pedogenic carbonate is represented by the equation (Cerling, 1991a; Kump, 2007)

$$
\delta_{\text{CARBONATE}} = \left( \frac{1}{R_{\text{PDB}}} \right) \left( S \left( \frac{D_S}{D_{13}} \right) \cdot \delta^* + C_A \cdot \delta_A^* \right) \left( S \left[ 1 - \left( \frac{D_S}{D_{13}} \right) \cdot \delta^* \right] + C_A \cdot \left( 1 - \delta_A^* \right) \right) * 1000 + 9.7
$$

$\delta_{\text{CARBONATE}} = \delta^{13}C$ value of the pedogenic carbonate

$R_{\text{PDB}} =$ ratio of $^{13}C/^{12}C$ in Pee Dee Belemnite standard, 0.0112372

$S =$ difference between soil and atmospheric pCO₂, values range from 5000-10000ppm (Bowen and Beerling, 2004)

$$
\left( \frac{D_S}{D_{13}} \right) =$ the ratio of soil CO₂ and $^{13}$CO₂ diffusion rates, since most soil CO₂ is $^{12}$CO₂ it diffuses faster than $^{13}$CO₂, 1.0044

$\delta_{S^*, \delta_A^*} = \delta^{13}C$ of soil respired and atmospheric CO₂ (approximately -25 and -6 in the model)

These values are converted to actual isotopic ratios using the equation

$$
\delta^* = \frac{R_{\text{PDB}} \left( \frac{\delta}{1000 + 1} \right)}{1 + R_{\text{PDB}} \left( \frac{\delta}{1000 + 1} \right)}
$$
$C_A = \text{atmospheric pCO}_2 \text{ (ppm)}$

9.7‰ correction due to fractionation of carbon between CO$_2$ and CaCO$_3$

**Paleocene Eocene Thermal Maximum (PETM)**

The PETM was a short-lived global warming event that occurred at the boundary of the Paleocene and Eocene approximately 55 million years ago (Kennett and Stott, 1991). This warming resulted in global temperature increases of 5-10 degrees Celsius that increased steadily from the beginning of the event to peak 60kyr later (Bowen, 2004; Wing et al., 2005). The PETM has been associated with a rapid negative carbon isotope excursion which lasted for approximately 35 kyr, with an exponential recovery of $\delta^{13}C$ values lasting about 50kyr, increased ocean stratification (Higgins and Schrag, 2006), and mass extinctions of marine and terrestrial organisms (Pak and Miller, 1992).

Controversy has risen in the scientific community about the causes of the PETM. Some studies suggest that the global warming was triggered solely by the massive release of methane hydrate reservoirs (Dickens et al., 1997). Methane hydrate release would explain the negative excursion of carbon isotopes, however, because CH$_4$ has a short atmospheric residence time it does not suffice to explain the magnitude and extent of the temperature increases (Bowen, 2004). Because CO$_2$ has a much longer residence time, massive releases of organic CO$_2$ to the atmosphere in addition to methane has been proposed as a more probable cause for the events of the PETM (Bowen, 2004; Higgins and Schrag, 2006). This massive release of organic carbon has been used to help explain the 3‰ discrepancy between marine and terrestrial isotope records from the period (Fig. 1). Changes in ocean chemistry as a result of carbon forcing (Tripati and Elderfield, 2005; Zachos et al., 2006), a more humid climate (Bowen, 2004), and changes in the...
Figure 1. (Taken from Bowen et al., 2004)
(A) Shows marine Del C13 records from surface dwelling organisms - blue circles from the Southern Ocean, red squares are from the subtropical Pacific Ocean. (B) Del C13 record of paleosol carbonates from northern Spain (blue circles), Hunan, China (red squares), and Wyoming, USA (green diamonds). (C) Shows temperature anomalies for the sites in A calculated from Del O18 and Mg/Ca records. (D) Normalize composite carbon isotope curves for paleosol carbonates in green and planktonic foraminiferal carbonate (in blue) highlighting the discrepancy in the isotopic signature of the ocean and the terrerestrial biosphere.
composition of land plants (Bowen, 2004; Wing et al., 2005) are also thought to have played roles in characterizing the nature of the isotope excursion. The use of a carbon cycle model to simulate the effect of massive releases of organic carbon to the atmosphere in the present may provide insight about the causes and effects of the PETM.

**MODEL SETUP**

I began with Dave Bice’s long term carbon cycle model (Bice, 2008) which had many of the reservoirs and flows discussed above. In order to properly investigate the effects of anthropogenic carbon forcing on pedogenic carbonate isotopic signatures I revised the model, adding complexity. To the general model I added a litter reservoir and its corresponding processes of runoff to the warm and cold surface oceans, burial of carbon into the soil reservoir, and litter respiration to the atmosphere. This addition resulted in the simplified model displayed in Figure 2, which shows each reservoir and the direction and destination of its principle flows. For all final equations and a representation of the complete model with conversion factors see Appendix 1 and 2.

The initial value for each of the model’s reservoirs is given in Table 1. The initial values are sensitive not only because they must reflect the reality of pre-industrial carbon cycle conditions, but also because they must be compatible with the model equations and all other initial values in order for the model to run in steady state. A correct initial value for atmospheric carbon is particularly important because it has such a direct impact on so many other reservoirs. The effects of anthropogenic carbon emissions are first seen in the atmosphere, and thus the initial value must correspond to accepted pre-industrial standards if the results of the model are to be applicable to interpretations of climate
Figure 2. Global carbon cycle reservoirs and fluxes in Gt C and Gt C/yr respectively. Arrows show origin and destination of primary fluxes, open circles describe the process determining the magnitude of the flux. Emissions and land use changes are both shown with arrows indicating points of entry into the global carbon cycle.
change. A beginning atmosphere between 600 and 700 GtC is generally accepted in the carbon cycle modeling literature (Bolin et al., 1979; IPCC, 1994).

Values for the remaining reservoirs display greater ranges in the carbon cycle literature. While some of this range is due to incomplete records and data gathering, the differences in values come largely from discrepancies in the reservoirs across space and time. The constantly changing nature of these reservoirs as well as their natural variations across ecosystems and climate regions make precise measurements of both reservoirs and fluxes nearly impossible. The values chosen for the model fall within the range of values used in previous global carbon cycle models (Bice, 2008; Bolin et al., 1979; Ehleringer et al., 2000a; IPCC, 2001; Kwon and Schnoor, 1994; Siegenthaler and Sarmiento, 1993).

**TABLE 1. INITIAL MODEL RESERVOIR VALUES**

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Initial Value (GtC/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td>600</td>
</tr>
<tr>
<td>Land Biota</td>
<td>610</td>
</tr>
<tr>
<td>Litter</td>
<td>80</td>
</tr>
<tr>
<td>Soil</td>
<td>1500</td>
</tr>
<tr>
<td>Warm Surface Ocean</td>
<td>616.549625</td>
</tr>
<tr>
<td>Cold Surface Ocean</td>
<td>352.543845</td>
</tr>
<tr>
<td>Deep Ocean</td>
<td>38000</td>
</tr>
</tbody>
</table>

The next revision to the model added $\delta^{13}C$ reservoirs for the existing carbon reservoirs in order to track isotope changes through each. Isotope changes in the reservoirs were calculated using the isotope equation described above. The equations can be viewed in Appendix 1. Initial values for these reservoirs were chosen in order to keep
the model in steady state while including realistic fractionation factors. A few of the isotope reservoirs did not start at accepted pre-industrial $\delta^{13}C$ values. Atmosphere, which has a typically accepted value of -6‰ (Sharp, 2007) started at 0.16. Though these values were not strictly desirable, the model still ran in steady state, and isotope values were merely measured as isotope excursions instead of actual $\delta^{13}C$ values. All fractionation factors are listed in Table 2. Fractionation factors, like initial values, have widely acceptable ranges due to their defining parameters that are controlled by different ecosystems and climate regions, and their resulting natural seasonal and annual fluctuations. The fractionation values chosen follow closely those found in Sharp’s isotopic description of the carbon cycle (Sharp, 2007)

<table>
<thead>
<tr>
<th>Fractionating Process</th>
<th>$\delta^{13}C$ Fractionation Shift (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photosynthesis</td>
<td>-25</td>
</tr>
<tr>
<td>Fossil Fuel Burning</td>
<td>-23</td>
</tr>
<tr>
<td>Volcanic Emissions</td>
<td>-6</td>
</tr>
<tr>
<td>WarmOc-Atm Transfer</td>
<td>-9</td>
</tr>
<tr>
<td>Atm-WarmOc Transfer</td>
<td>-2</td>
</tr>
<tr>
<td>ColdOc-Atm Transfer</td>
<td>-2</td>
</tr>
<tr>
<td>Atm-ColdOc Transfer</td>
<td>-9</td>
</tr>
<tr>
<td>WarmOc Biological Pump (Organic Carbon Transfer)</td>
<td>-32</td>
</tr>
<tr>
<td>ColdOc Biological Pump (Organic Carbon Transfer)</td>
<td>-32</td>
</tr>
</tbody>
</table>

Figure 3 displays the portion of the model that describes isotope change in the deep ocean reservoir. Downwelling, carrying the isotopic signature of the cold surface
Figure 3. Model of the isotopic signature of the deep ocean reservoir. Colored boxes represent reservoirs and their corresponding Del C13 reservoirs. Inflows are indicated by black circles. Downwelling carries the isotopic signature of the cold surface ocean. Both organic carbon depositions (org c dep wo and org c dep co) fractionate -32 per mil. Outflows, deposition and upwelling, shown in pink, leave the reservoir without changing the isotopic composition. All inflows and outflows feed into Isotope Change DO, calculating isotope change at each time step in the model. This flows directly into Del C13 Deep Ocean giving the actual Del C13 value for the deep ocean.
ocean and organic carbon coming from both the cold and warm surface ocean reservoirs
with a fractionation of -32‰ make up the inflows to the deep ocean reservoir (Kump,
1991). Deposition and upwelling both flow out of the deep ocean reservoir with no
impact on the reservoir’s isotopic signature.

Figure 4 displays the isotopic model for the warm surface ocean. Runoff carrying
the isotopic signature of the litter reservoir and upwelling from the deep ocean reservoir
are the primary simple inflows to the warm surface ocean isotopic reservoir. Ocean
atmosphere exchange as discussed previously is a complex process controlled by a
variety of parameters. In terms of isotopes, the signature of CO₂ changes depending on
which direction it is flowing. If CO₂ is transferred from the warm surface ocean to the
atmosphere (which is the usual case) the isotopic signature of the flow is -9‰, if CO₂ is
flowing from the atmosphere into the warm surface ocean, this CO₂ carries an isotopic
signature of -2‰. Advection flows out of the reservoir without affecting the isotopic
signature, while the transfer of organic carbon from the warm surface ocean to the deep
ocean has a fractionation factor of -32‰ (Walker, 1991).

Figure 5 shows the isotopic model for the cold surface ocean. Runoff from the
litter reservoir and advection carrying the δ¹³C signature of the warm surface ocean
constitute the simple inflows. Exchange between the atmosphere and the cold surface
ocean functions like that of the warm surface ocean. Downwelling out of the cold surface
ocean δ¹³C reservoir has no affect on the reservoir’s isotopic signature, while the transfer
of organic carbon to the deep ocean again has a fractionation factor of -32‰ (Walker,
Figure 4. Model of the isotopic signature of the warm surface ocean reservoir. Colored boxes represent reservoirs and their corresponding Del C13 reservoirs. Upwelling and Runoff 2 are inflows indicated by black circles. Upwelling carries the isotopic signature of the deep ocean, while Runoff 2 enters the warm surface ocean with the isotopic signature of the litter reservoir. All outflows are shown by pink circles. Advection flows with no fractionation to the cold surface ocean without altering the isotopic composition of the warm surface ocean. Org c dep wo flows out with a fractionation of -32 per mil. WO Atm Change is a special convertor that gives an isotopic value of -9 if CO2 is transferred from the warm surface ocean to the atmosphere and -2 if the transfer is reversed. All inflows and outflows feed into Isotope Change WSO, calculating isotope change at each time step in the model. This flows directly into Del C13 Warm Surf Oc giving the actual Del C13 value for the warm surface ocean.
Figure 5. Model of the isotopic signature of the cold surface ocean reservoir. Colored boxes represent reservoirs and their corresponding Del C13 reservoirs. Advection and runoff are both simple inflows, indicated by black circles, carrying the isotopic signatures of the warm surface ocean and litter reservoirs respectively. CO Atm Change is a convertor that describes the movement of CO2 between the atmosphere and cold ocean. Initially, carbon will be transferred from the atmosphere to the cold ocean with an isotopic signature of -2 per mil. Downwelling and org c dep co are both outflows represented by pink circles. Downwelling flows with no fractionation to the deep ocean, without altering the isotopic composition of the cold surface ocean. Org c dep co flows to the deep ocean with a fractionation of -32 per mil. All inflows and outflows feed into Isotope Change CSO, calculating isotope change at each time step in the model. This flows directly into Del C13 Cold Surf Oc giving the actual Del C13 value for the cold surface ocean.
Figure 6 depicts the isotope model for the litter reservoir, which had an initial value of -24.84‰. Litter fall carrying the isotopic signature of the land biota is the only inflow to the isotope reservoir. Litter respiration, burial, and runoff to both the warm and cold surface oceans flow out of the $\delta^{13}$C litter reservoir without affecting the isotopic signature.

Figure 7 shows the isotope model for the land biota reservoir, which also has an initial value of -24.84‰. Photosynthesis from the atmosphere flows into the reservoir with a fractionation factor of -25‰. This fractionation factor does not take into account the difference in photosynthesis between $C_3$ and $C_4$ plants, and assumes an entirely $C_3$ ecosystem (Cerling, 1991b; Sharp, 2007). Below ground additions to the soil, litter fall, and plant respiration to the atmosphere are all outflows that do not fractionate, and thus do not affect the isotopic signature of the land biota.

Figure 8 displays the isotope model for the soil reservoir, which also begins at a value of -24.84‰. Inflows to the reservoir include burial which has the isotopic signature of the litter reservoir and below ground additions from the land biota. Soil respiration from the soil to the atmosphere does not fractionate and has no resulting effect on the isotopic signature of the soil reservoir.

Figure 9 shows the isotope model for the atmosphere reservoir. Litter, soil, and plant respiration all flow into the atmosphere reservoir carrying the isotopic signature of their respective reservoirs. Transfers between the atmosphere and the warm and cold surface oceans function as described above. Volcanoes enter the atmosphere with a $\delta^{13}$C value of -6‰ (Sharp, 2007). Both emissions and land use changes enter the atmosphere with a $\delta^{13}$C value of -23‰ (Sharp, 2007; Stuvier et al., 2000).
Figure 6. Model of the isotopic signature of the litter reservoir. Colored boxes represent reservoirs and their corresponding Del C13 reservoirs. Litter fall is the only inflow, indicated by a black circle. Litter fall carries the isotopic signature of the land biota. Burial, Runoff 1, Runoff 2, and Litter Respiration, all outflows shown by pink circles, flow with no fractionation to the soil, cold surface ocean, warm surface ocean, and atmosphere respectively without altering the isotopic composition of the litter. All inflows and outflows feed into Isotope Change Litter, calculating isotope changes at each time step in the model. This flows directly into Del C13 Litter giving the actual Del C13 value for the litter.
Figure 7. Model of the isotopic signature of the land biota reservoir. Colored boxes represent reservoirs and their corresponding Del C13 reservoirs. Photosynthesis is the only inflow, indicated by a black circle. Photosynthesis enters from the atmosphere, and fractionates this isotope ratio -25 per mil. Litter fall, Below Ground, and Plant Respiration, all outflows shown by pink circles, flow with no fractionation to the litter, soil, and atmosphere respectively without altering the isotopic composition of the land biota. All inflows and outflows feed into Isotope Change LB, calculating isotope change at each time step in the model. This flows directly into Del C13 Land Biota giving the actual Del C13 value for the land biota.
Figure 8. Model of the isotopic signature of the soil reservoir. Colored boxes represent reservoirs and their corresponding Del C13 reservoirs. Burial and below ground are inflows indicated by black circles. Burial carries the isotopic signature of the litter reservoir and below ground has the isotopic signature of the land biota. Soil respiration, the only outflow, shown in pink, leaves the reservoir without changing the isotopic composition. All inflows and outflows feed into Isotope Change Soil, calculating isotope change at each time step in the model. This flows directly into Del C13 Soil giving the actual Del C13 value for the soil.
Figure 9. Model of the isotopic signature of the atmosphere. Colored boxes represent reservoirs and their corresponding Del C13 reservoirs. Black circles indicate flows into the atmosphere, pink circles represent flows out of the atmosphere. These flows and the Del C13 values of the reservoirs they originated in are used to calculate Isotope Change Atm, which flows into the Del C13 Atmosphere reservoir, recording actual C13 values. Photosynthesis has a fractionation of -25 per mil which is taken into account as it flows out. Atm WO Change and Atm CO change are special convertors designed to give an isotopic value of -2 if the atmosphere is transferring CO2 to the ocean, and -9 if CO2 travels from the ocean to the atmosphere.
The final revision to the model was the development of $\delta^{13}C$ convertors that tracked the high and low estimates of pedogenic carbonate isotopic signatures. Figures 10A and 10B show the pedogenic isotope models. The $\delta^{13}C$ value is calculated by the equation described above for pedogenic carbonates. The low estimate uses an S value of 5000 ppm, while the high estimate calculates the isotopic signature using an S value of 10000 ppm.

Once the final model was complete it was run in steady state for 10000 years, to ensure that all initial values remained constant. Following this test of the model, four different anthropogenic perturbation scenarios were developed to test the effect of releases of different amounts of carbon over different time ranges. These emission scenarios are displayed graphically in Figure 11. Each emission scenario begins in the year 1850 with real carbon emission data from the Carbon Dioxide Information Analysis Center through 2004 (Marland et al., 2007). These emissions total 38.675 Gt over the 154 year period put into the model as an average rate of emissions over every ten years. Scenario A is based off of the Intergovernmental Panel on Climate Change (IPCC) A1V1 Minicam emission scenario (IPCC Working Group III, 2008). Over 400 years a total of 318 Gt of carbon are emitted. Scenario B emits 414.98 Gt of Carbon over the course of 800 years. Scenario C is based off of the IPCC A1C A1M scenario (IPCC Working Group III, 2008) and over the course of 350 years emits 746.97 Gt of carbon. Scenario D combines Scenario B with land use changes. These land use changes were calculated as one third the emissions or 138.33 Gt of carbon, resulting in total carbon emissions for Scenario D of 553.31 over 800 years. Each scenario was run in the model for 3000 years,
Figure 10. Model of pedogenic carbonate isotopic signature convertor. The Del C13 value is determined by the isotopic signature of the soil and atmosphere reservoirs, the diffusion rate of soil, and the relative concentrations of CO2 in the atmosphere and soil reservoirs. (A) The high estimate uses a difference between soil and atmospheric pCO2 (SPCO2 APCO2 Hi) value of 10000 ppm. (B) The low estimate uses a difference between soil and atmospheric pCO2 (SPCO2 APCO2 Lo) value of 5000 ppm. B uses convertors already established in A and thus is not directly connected to Del C13 Atmosphere and Soil in the model.
Figure 11. Graph shows 4 different emissions scenarios. A emits 318 Gt C over 400 years, B emits 414.98 Gt C over 800 years, and C emits 746.97 Gt C over 350 years. D combines fossil fuel burning from Scenario B with land use changes for total emissions of 553.31 over 800 years. The first 154 years of each scenario is the same and based on real carbon emissions (Marland et al., 2007) with model year 0 representing 1850.
with model year 0 corresponding to the year 1850. The differential equation solver Runga Kutta 2 was used with a time step of 0.1 years.

RESULTS

Scenario A

Scenario A, based off of IPCC A1V1 Minicam emission scenario emitted a total of 318 Gt of carbon over a 400 year period. Scenario A represents a moderate input of anthropogenic carbon to the atmosphere over a moderate period of time. This scenario had peak emissions of 17.6 GtC/yr for a 10 year period between model year 240 and 250. The model was run for 3000 years. Figure 12 shows the change in global temperature during the simulation. Scenario A shows a small peak in temperature change of 4.2°C between years 278 and 285. Temperature change decreases slightly following this peak and then proceeds to increase uniformly ending at a total temperature change of 9.3°C at the end of 3000 years.

Figures 13A and 13B show graphs of changes in the carbon and CO₂ concentrations of the atmosphere for each scenario. Scenario A causes overall increases in atmospheric carbon. Starting at 600 GtC or 280 ppm, Scenario A causes rapid increases in atmospheric carbon until the year 281 where the atmosphere peaks at 1500.02 GtC. An approximately 100 year decrease follows this peak, eventually increasing consistently to a final level of 2592.63 GtC or 1209.89 ppm at the end of 3000 years. In addition to affecting the amount of carbon in the atmosphere reservoir, Scenario A also caused an excursion in the atmospheric isotopic signature (Fig. 14). The carbon isotopes in the atmosphere become increasingly depleted in $^{13}$C through the course of the simulation. The change in δ$^{13}$C values is rapid during the first 250 years of the
Figure 12. Graph shows global temperature over the 3000 year model run. Scenario A is pictured in blue/square, Scenario B is in red/triangle, Scenario C is light blue/circle, and Scenario D is green/star. All scenarios are characterized by temperature increases. The fastest initial increase is seen in Scenario C with a temperature increase of 8.21 degrees Celsius during years 320-324. Scenario A shows the highest temperature increase overall ending the simulation at an increase of 9.3 degrees Celsius.
Figure 13. Graphs showing changes in the carbon and CO2 concentrations of the atmosphere for each emission scenario. (A) shows the concentration of CO2 in the atmosphere in parts per million (B) shows the mass of carbon in the atmosphere reservoir in gigatons. Both graphs show the largest increases in atmospheric carbon under the forcing regime of Scenario A.
Figure 14. Shows the excursion of carbon isotopes in the atmosphere reservoir for each scenario. The largest initial negative excursion occurs under the forcing of Scenario C. The largest overall excursion occurs during Scenario A with ending isotope shift values of -8.59 per mil. Scenario B and D differ significantly due to the added effect of isotopically light land use changes in Scenario D. The initial rapid excursion in D indicates the importance of soil disruption (through agriculture and development) relative to fossil fuel burning in determining total anthropogenic carbon emissions during the period immediately following the Industrial Revolution.
simulation and peaks at a change of -3.89‰ during model year 269. This peak is followed by a rapid decrease in level of $\delta^{13}C$ change until model year 370 at which point the isotope shift becomes increasingly negative until it reaches a final value of -8.59‰ at the end of 3000 years.

Figure 15 shows the changes in the three ocean reservoirs with respect to the magnitude of carbon in the reservoirs and the isotopic excursion found in each. Scenario A causes increases in the magnitude of each reservoir. The increase in the deep ocean reservoir is rapid and relatively linear ending with 59529.11 Gt C in the deep ocean reservoir (Fig. 15A). The increases caused by Scenario A in the cold surface ocean are more gradual, and a slight peak is visible at model year 284 with 418.34 Gt C in the reservoir. The peak is followed by steady gradual increases in the magnitude of carbon with a value of 602.18 Gt C in the cold surface ocean reservoir at the end of the simulation (Fig. 15C). The trend of Scenario A in the warm surface ocean shows a similar peak at model year 284 at a reservoir of 639.57Gt C. This peak is also followed by a gradual increase. However, after reaching a peak of 640.5 Gt C at 2704, the value of the warm surface ocean reservoir begins to decrease ending the simulation at a value of 633.32 Gt C (Fig. 15E). Isotopically, the deep ocean and the warm surface ocean behave similarly under the forcing of Scenario A. Both reservoirs undergo relatively linear increases in the magnitude of their isotopic shifts ending at values of -7.84 and -7.67 respectively (Fig. 15B, F). The isotopic signature of the cold surface ocean is similar to the isotopic shift of the atmosphere in response to Scenario A. The isotopic shift rapidly increases in magnitude peaking at an isotopic shift of -3.74‰ during model year 277.
Figure 15. (A, C, E) Show changes in the storage of carbon in the deep, cold surface, and warm surface oceans respectively in Gigatons of carbon. (B, D, F) Show corresponding changes in del C13 values for these reservoirs.
The isotopic shift gradually increases becoming more negative until it reaches the end of the simulation with an isotopic shift of -9.71‰ for the cold surface ocean (Fig. 15D). The effect of each scenario on the terrestrial carbon cycle is shown in Figure 16. The land biota reservoir shows relatively constant moderate increases in total carbon throughout the simulation, with the exception of a small peak at year 300. Under the influence of Scenario A, the land biota reservoir reaches a final value of 991.77 Gt C (Fig. 16A). Photosynthesis is similarly affected, and shows general increases with a slight peak at year 278, ending the simulation with 162.71 Gt C caught up in photosynthetic processes (Fig. 16E). Scenario A decreases the magnitude of carbon in the soil reservoir. The initial decrease is rapid with a local minimum of 1370.44 Gt C occurring during model year 297. Following a slight increase, the amount of carbon in the reservoir decreases linearly ending at a value of 1200.61 Gt C (Fig. 16B). Soil respiration during this scenario increases in an identical pattern to photosynthesis. At the end of the simulation soil respiration is at 43.8 Gt C (Fig. 16F). The effect of Scenario A on the isotopic signature of the land biota and soil reservoirs is nearly the same. Both undergo rapid initial excursions reaching local minima of -3.88‰ and -3.55‰ at year 274 and 305 respectively. These dips are followed by rapid decreases in the magnitude of the isotopic shifts before a steady negative isotope shift begins to occur that carries out to the end of the simulation ending with an isotopic shift of -8.57 for the land biota and -8.52‰ for the soil reservoir (Fig. 16C, D).

Figure 17 shows the high and low estimates for the isotopic signature of the pedogenic carbonates for each scenario. Scenario A’s affect on the isotopic shift in pedogenic carbonates displays a similar pattern to that of the soil and land biota, though
Figure 16. (A) and (B) show changes in the land biota and soil carbon reservoirs in Gigatons of carbon for each scenario. (C) and (D) show shifts in the isotopic signatures of the land biota and soil reservoirs. (E) and (F) show changes in photosynthesis and soil respiration, two processes that show the effect of CO2 fertilization.
Figure 17. Shows shift in Del C13 of pedogenic carbonates. For each scenario upper estimates are given with open symbols, and lower estimates are given with closed symbols. Scenario A cause the overall greatest shift in the isotopic signature of pedogenic carbonates, ending with a shift range of -5.63 to 6.89 per mil. Scenario C shows the greatest initial change in isotopic signature. Scenario B and D differ in the graph showing the increased importance of land use changes when investigating isotope changes as opposed to the magnitude of carbon reservoirs.
the magnitude of the overall shift is somewhat smaller. Both high and low estimates begin with zero isotope shift, which rapidly becomes negative reaching local minima of -2.8‰ and -2.18‰ around model year 320. This rapid increase in the magnitude of isotopic shift is followed by an equally rapid decrease for about 100 years before a continuous rate of moderate shift makes the isotopic signature of the pedogenic carbonates lighter, ending with a shift range from -5.63 to -6.89‰.

**Scenario B**

Scenario B emitted a total of 414.98 Gt C over an 800 year period. This scenario was intended to represent very moderate carbon emissions over a long period of time (Fig. 11). Scenario B peaked between model years 170 and 190 with total emissions of 15.647 GtC/yr during this 20 year period. Emissions tapered off to between 3 and 7 GtC/yr after model year 290. Scenario B shows a small peak in global temperature change of 3.26 °C during year 228 and 229. Following this peak there is a slight relaxation of the temperature change. Fluctuations in temperature change occur 500 years into the simulation at which point temperature increases gradually to reach a maximum of 5.48 °C at the end of the simulation (Fig. 12).

Scenario B also had a positive effect on levels of carbon in the atmosphere. Like the other scenarios, B shows a rapid increase in atmospheric carbon during the first 250 years of the simulation. B peaks during year 228 with a total of 1297.61 Gt C present in the atmosphere reservoir. This peak is followed by a shallow dip followed by a gradual increase at year 375. The amount of carbon continues to increase gradually until the end of the simulation with a final atmosphere reservoir of 1773.93 Gt C or 827.84 ppm (Fig. 13A, B). Scenario B has the smallest immediate effect on the isotopic signature of the
atmosphere. The isotope excursion reaches a low peak of -3.01‰ during model year 218.
The isotope shift fluctuates becoming more negative and more positive alternately until
model year 665 when the isotopic signature of the atmosphere steadily becomes more
depleted with respect to $^{13}$C. Scenario B ends with an isotopic shift of -4.84‰ over the
course of 3000 years (Fig. 14).

Scenario B also has positive effects on the magnitude of carbon stored in the
ocean reservoirs and results in negative isotope excursions in all three ocean reservoirs.
The carbon increase in the deep ocean is relatively linear and shows a gradual increase in
the deep ocean reservoir to a final value of 47304.17 GtC (Fig. 15A). Increases in the
cold and warm surface oceans both show slight peaks around 250 years. The initial
increase for the warm surface ocean is much faster. Gradual increases characterize both
reservoirs following these small peaks ending at 458.71 Gt C in the cold surface ocean
and 644.99 Gt C in the warm surface ocean (Fig. 15C, E). Both the deep ocean and the
warm surface ocean show similar isotopic trends. Scenario B causes continuous gradual
increases in the magnitude of the isotope shift, resulting in reservoirs depleted in $^{13}$C by
-4.42‰ in the deep ocean and by 4.36‰ in the warm surface ocean (Fig. 15B, F). The
cold surface ocean also shows an overall increase in the negative shift of isotopic
signatures. This overall trend is broken up by positive and negative fluctuations during
the first 800 years of the simulation, ending finally with an isotopic of -5.42‰ in the cold
surface ocean reservoir (15D).

Scenario B causes overall increases in the amount of carbon utilized in
photosynthesis and soil respiration with a corresponding increase in the land biota
reservoir and a decrease in the soil reservoir. Both reservoirs show similar negative
isotope excursions. In Scenario B, modest increases are seen in the amount of carbon stored in the land biota. An initial rapid increase for about 300 model years is seen before the increase becomes relatively linear and gradual ending with a value of 861.69 Gt C in the land biota (Fig. 16A). Photosynthesis shows similar moderate increases, though the rate of change for the first 300 years of the model is much more rapid. After slight fluctuations, photosynthesis increases linearly reaching an ending value of 141.32 Gt C (Fig. 16E). The soil reservoir undergoes a decrease in the amount of stored carbon during Scenario B, showing similar fluctuations until model year 800 at which point the decrease is linear and gradual ending at 1318.34 Gt C (Fig. 16B). Soil respiration increases in a pattern identical to photosynthesis and ends at a value of 38.63 Gt C (Fig. 16F). The isotopic shift caused in both the land biota and soil reservoirs as a result of Scenario B also follows the same patterns. Initial rapid decreases occur for the first 270 years of the model at which point small positive and negative fluctuations occur. At model year 448, the isotopic shift becomes consistently and increasingly negative ending at isotope shifts of -4.8‰ in the soil and -8.57‰ in the land biota (Fig. 16C, D).

In Scenario B the change in the isotopic signature of pedogenic carbonates behaves similar to the shifts found in the soil and land biota reservoirs. The high and low estimates follow identical patterns of change. An initial rapid decrease in the first 300 years of the model is followed by slight positive and negative fluctuations. A continuous relatively linear decrease begins at model year 536, with pedogenic carbonates ending the simulation with isotope shifts between -2.98 and -3.81‰ (Fig. 17).

**Scenario C**
Scenario C was based off of the IPCC A1C A1M scenario, and emitted 746.97 Gt of carbon over 350 years. This scenario represented rapid release of large quantities of carbon. Scenario C also resulted in increased global temperatures. Changes in temperature peaked between 320 and 324 with a global temperature change of 8.21°C. This dramatic peak is followed by rapidly decreasing temperature changes which plateau at 4.19°C 528 years into the simulation (Fig. 12).

Changes in atmospheric carbon are also caused by the perturbations of Scenario C. Atmospheric levels of carbon increase dramatically from their starting value of 600 Gt C, peaking in Scenario C at 2358.96 Gt C during model year 322. This rapid increase is followed by an equally fast decrease at which point atmospheric carbon and CO₂ remain constant for the remainder of the simulation, ending with 1497.99 Gt C in the atmosphere or 669.06 ppm of CO₂ (Fig. 13A, B). Scenario C also causes rapid changes in the isotopic signature of the atmosphere. An isotopic shift of -8.19‰ is reached during model year 318 and is sustained for 8 years before the magnitude of the shift rapidly decreases, leveling off to a constant shift of -3.3 from 2744 to the end of the simulation (Fig. 14).

Scenario C causes increases in the amount of carbon stored in all three ocean reservoirs and also instigates a negative isotope excursion in these reservoirs. The amount of carbon in the deep ocean reservoir increases rapidly and then levels off to constant value of 44149.79 Gt C (Fig. 15A). Both the cold and warm surface ocean reservoirs undergo similar patterns of change, with rapid increases and decreases occurring within the first 500 years of the simulation. The warm surface ocean peaks at 637.73 Gt C during model year 329 and the cold surface ocean peaks at 559.77 Gt C
during model year 327. Both reservoirs then rapidly decrease reaching a constant amount of carbon for the remainder of the simulation ending at 632.07 Gt C and 418.31 Gt C respectively (Fig. 15C, E). The isotopic signatures of the deep and warm surface ocean undergo almost identical changes as a result of Scenario C. Isotopic shifts undergo rapid negative changes in the first 500 years of the model and then level out to a shift of -3.32‰ for the deep ocean and -3.28‰ for the warm surface ocean (Fig. 15B, F). The isotopic shift in the cold surface ocean undergoes more dramatic fluctuation reaching a minimum of -8.55‰ during model year 354. The isotope shift rapidly becomes less negative before reaching a constant value of -3.7‰ from model year 600 to the end of the simulation (Fig. 15D).

Scenario C has less overall effect on the terrestrial carbon cycle than the other perturbation scenarios. Mild increases are seen in the land biota reservoir, photosynthesis, and soil respiration. The soil reservoir decreases in magnitude, while the isotopic signature of both the land and soil reservoirs shows a negative excursion. The land biota reservoir shows an initial rapid increase up to 954.98 GtC during model year 356. This increase is followed by a rapid decrease which levels out and remains constant for the rest of the simulation at 814.25 Gt C (Fig. 16A). Photosynthesis shows similar trends of increased carbon and has a value of 133.48 at the end of Scenario C (Fig. 16E). The soil reservoir undergoes similar patterns of change, but in the opposite direction. The soil reservoir is characterized by an initial rapid decrease in magnitude of carbon reaching a minimum of 1230.95 Gt C in model year 355. The soil reservoir rapidly increases and then remains constant with an ending value of 1366.99 Gt C (Fig. 16B). Soil respiration follows an identical pattern to photosynthesis with a peak of 42.68 Gt C during model
year 314-317, and an ending value of 36.73 Gt C (Fig. 16F). The isotopic signature shift of both the land biota and soil reservoirs behave similarly. An initial rapid negative excursion of both isotopes occurs, with minima of -7.92‰ at model year 360 for soil and -8.17‰ at model year 330 for the land biota. This extreme decrease in isotopes is followed by an equally rapid increase which then levels off and remains constant for the duration of the simulation at values of -3.3‰ for both the soil and the land biota reservoirs (Fig. 16C, D).

The isotopic shift in pedogenic carbonates follows a pattern similar to that found in the soil and land biota reservoirs. Scenario C causes initial extremely rapid negative isotope excursions, bottoming out at -6.55‰ and -5.46‰ for the high and low estimates. The isotopic shift then becomes rapidly less negative followed by a leveling out at model year 983. The isotopic shift remains constant for the rest of the simulation at -2.5‰ and -1.84‰ for the upper and lower estimates (Fig. 17).

Scenario D

Scenario D combines the anthropogenic carbon emissions from Scenario B with land use changes. Land use changes were estimated as one-third of total yearly carbon emissions, resulting in 138.33 Gt of carbon, making total carbon release during Scenario D 553.31 Gt C over 800 years. This scenario, like B, was created to observe the effects of moderate carbon release over a long period of time while also looking at the effects of land use changes. The effect of scenario D on global temperature mirrors that of Scenario B. Scenario D has a slightly larger, earlier peak in global temperature change causing warming of 3.48°C between 224 and 228. Slight fluctuations follow the peak
before temperature change gradually increases to 5.49°C at the end of the simulation (Fig. 12).

Trends of increasing atmospheric carbon concentrations continue with Scenario D. Increases are almost identical to those found in Scenario B. Scenario D causes overall slightly higher atmospheric carbon concentrations and has a slightly larger, earlier peak. Scenario D causes rapid increases in atmospheric carbon that peak at year 226 with 1345.75 Gt C. The eventual increase that follows this peak is almost identical to the slope of Scenario B, but ends at a slightly higher value of 1775.89 Gt C or 828.75 ppm (Fig. 13A, B). Scenario D causes a similar pattern of change to the isotopic composition of the atmosphere as those seen in Scenario B, though the magnitudes of the shifts predicted from Scenario D are larger. A rapid decrease is seen in the isotopic signature of the atmosphere under the influence of Scenario D reaching a shift of -3.06 during model year 461. The magnitude of this shift decreases rapidly, undergoes minor fluctuations, and in year 807 begins to increase gradually to a final shift of -6.21‰ (Fig. 14).

Scenario D also causes increases in the amount of carbon found in the three ocean reservoirs and shows a negative isotope excursion in each. The patterns of increase in the deep, cold surface, and warm surface oceans are nearly identical to those in Scenario B with increases being generally moderate and relatively linear. The oceans end at values of 47334.25, 459.01, and 635.01 Gt C respectively (Fig. 15A, C, E). The isotopic signatures of the ocean reservoirs also change identically to Scenario B with the magnitude of the shifts being slightly higher in Scenario D. The deep and warm surface oceans are characterized by relatively continuous increasing magnitudes of negative
isotopic shifts ending at shifts of -5.67‰ in the deep ocean and -5.61‰ in the warm surface ocean (Fig. 15B, F). The isotopic signature of the cold surface ocean shows more dramatic fluctuation reaching a local minimum of -3.8‰ between years 207 and 218. The final isotope shift for the cold surface ocean is -6.77‰ (Fig. 15D).

The change in the terrestrial carbon cycle as a result of Scenario D shows more carbon in the land biota reservoir, photosynthesis, and soil respiration. The amount of carbon in the soil decreases, and isotopes across the cycle show negative excursions. The land biota shows a general trend of moderate increase, with a slightly more rapid rate of change during the first 250 years of the simulation. The ending value for the land biota reservoir is just slightly below that of Scenario B with 852.92 Gt C stored in the land biota (Fig 16A). Photosynthesis shows similar trends of increase that result in 141.37 Gt C caught up in photosynthesis at the end of the simulation (Fig. 16E). The soil reservoir shows the opposite effect. As Scenario D is run, the amount of carbon in the soil decreases rapidly for the first 300 years of the simulation, and then achieves a steady downward slope ending with a value of 1295.58 Gt C in the soil reservoir (Fig. 16B). Soil respiration behaves much like photosynthesis undergoing initial rapid increases that taper off to a steady positive moderate linear slope with soil respiration ending at 38.24 Gt C (Fig 16F). The isotopic signatures of both the soil and the land biota become more negative as a result of Scenario D. Like the trend in the soil reservoir itself, the initial decrease in isotope values is rapid, undergoes minor fluctuations and then begins a steady downward trend ending with isotope shifts of -6.2‰ in the land biota and -6.16‰ in the soil reservoir (Fig. 16C, D).
The isotopic shift found in pedogenic carbonates during Scenario D are similar to those found in Scenario B and also to the shifts recorded in the soil and land biota reservoirs during Scenario D. The isotope shifts undergo initial rapid negative excursions reaching a high estimate of almost -3‰ at year 300. Mild positive and negative fluctuations characterize the next portion of the excursion until model year 866 when the isotope shift begins to move steadily downward at a moderate rate. The final values for pedogenic isotopes are -5.17‰ for the high estimate and -4.35‰ for the low estimate (Fig. 17).

**DISCUSSION**

The model results indicate the importance of the total magnitude of carbon released, the rate at which it is released, and the total length of time for which emissions are present in predicting the effect of anthropogenic carbon emissions on the carbon cycle, global temperature, and carbon isotopes. We would expect to see scenarios that released the greatest amount of carbon over the shortest period of time to have the largest forcing effect on the carbon concentration of the atmosphere, while scenarios that emitted less carbon over a long period of time to force more gradual changes in the carbon cycle.

Scenario A which released 318 Gt of carbon over 400 years at moderate levels, never emitting less than 7 GtC/yr, shows overall the largest increases in the global temperature at the end of 3000 years. Strong initial peaks in temperature change show direct responses to the peak in the level of emissions. The temperature continues to increase steadily after the cessation of emissions indicating the importance of CO₂ residence time in determining climate change (Fig. 12). This same trend is seen in the magnitude of carbon in the atmosphere. Graphs of the atmosphere reservoir also show
initial peaks as a direct response to carbon forcing. These peaks correspond to the highest levels of emissions during which the excess carbon forcing prevented the carbon cycle from reestablishing equilibrium and storing carbon among its reservoirs (Fig. 13A,B).

Scenario B and D, due to their similar effects on temperature and atmosphere will be treated together. Scenario B and D released 414.98 and 553.31 Gt C respectively over the course of 800 years, with the releases being usually between 3 and 5 GtC/yr. Global temperature increases consistently throughout the scenarios, showing only very slight fluctuations in response to relatively small peaks in the emissions scenarios (Fig. 12). The overall increase is less than that seen in Scenario A, indicating the importance of the amount of carbon released per year in determining initial temperature perturbation. Increases in the carbon concentrations of the atmosphere follow similar patterns to those found in Scenario A, with a more gradual rate of increase in the magnitude of the reservoir (Fig. 13A, B). The almost identical results for B and D demonstrate the lack of significance of 1 or 2 GtC/yr over this long period of time.

Scenario C has the most immediate effect on global temperature and atmospheric concentrations of carbon and CO2. The sharp peaks during the high points of the emission scenarios again demonstrate the rapid effect of carbon forcing on the temperature and the atmosphere. The leveling off of both temperature and atmospheric CO2 are unexpected (Figs 12, 13A). These large quantities of carbon equaling 746.97 Gt of carbon over the course of 350 years seem likely to provoke the greatest effect on the carbon cycle. However, the limited amount of model run time restricts our ability to assess long term changes. It is possible that this leveling out is similar to the 100-300
year dips seen in Scenario A and B, and that due to the brevity of emission time, an increase will occur after 3000 years. This scenario does, however, point out the initial significance of both length of emission time in addition to levels of output per year.

The ocean reservoirs also serve as good indicators of the reaction time of the carbon cycle to anthropogenic forcing. In Scenario A, peaks in the surface reservoirs occur as a slightly delayed reaction to the peak in emissions (Fig. 15C, E). Lack of such a peak in the deep ocean (Fig. 15A) indicates the time required for carbon increases in the rest of the cycle to reach the deep ocean. The peak seen in the atmosphere is not absorbed into the deep ocean until after the emissions have ceased. The cold surface ocean shows lower levels of increase than the warm surface ocean, which is expected given the constant rate of photosynthesis dictated by the model settings. The warm surface ocean shows an interesting decrease perhaps indicating a change in the ocean atmosphere exchange, or an initial move toward reestablishment of steady state.

The oceans in Scenario B and D show similar trends to the ocean reservoirs observed in Scenario A, though the overall magnitude and rate of change is less. The deep ocean again shows almost no peak, indicating both lack of a strong peak in the emissions scenarios and a delay between emissions and uptake by the deep ocean (Fig. 15A). The rate of carbon increase in the cold surface ocean is slightly less than that of the warm surface ocean, again, due to the constant rate of photosynthesis. The warm surface ocean, while it shows no decrease at the end of the simulation does show a strong initial peak (Fig. 15C, E). The similarity between these two scenarios again displays the importance of amount of carbon per year in determining carbon cycle changes.
Scenario C again behaves somewhat unexpectedly. The deep ocean increases rapidly and levels off, while the two surface reservoirs undergo a rapid initial peak and decline before becoming constant (Fig. 15A, C, E). This does not display the expected delay for uptake in the deep ocean. The great magnitude of carbon and the rapid rate of emission may have caused carbon to be redistributed more quickly through the carbon cycle. Again, the short length of simulation could be obscuring the actual results of Scenario C.

The response of terrestrial carbon to anthropogenic forcing informs our interpretation of how accurate the carbon cycle model is. The expected carbon fertilization effect is clearly seen in Scenario A. The carbon stored in the land biota increases as does the rate of photosynthesis (Fig. 16A, E). Warmer climates promote the growth of plants, which in turn increases photosynthetic processes. This excess storage of carbon, however, is offset by the increased release of carbon through soil respiration (Fig. 16F). The soil, which currently functions as a net sink of carbon, experiences increased microbial activity and decomposition, releasing organic carbon to the atmosphere. This release causes an overall decrease in the amount of carbon stored in the soil reservoir (Fig. 16B). The largest decrease in the soil reservoir and increase in the land biota reservoir occur at the end of Scenario A, indicating the effect of moderate to high inputs of carbon each year for a moderate period of time.

The effect of Scenario B and D on the land biota and photosynthesis demonstrates a moderate state of carbon fertilization (Fig. 16A, E). The two scenarios however depict different versions of change in the soil reservoir and soil respiration. Scenario D causes much more rapid initial and overall greater decreases in the soil reservoir than Scenario B.
(Fig. 16B). Because Scenario D adds in land use changes which feed directly into soil respiration, this result makes sense. In addition to the effect of increased microbial activity and decomposition, excess organic carbon is released to the atmosphere through soil disruption and tree cutting. The initial rapid response correlates to the larger role of land use changes relative to fossil fuel burning in determining total anthropogenic carbon emissions immediately after the year 1850. Scenario C has the same directional effects on land biota, photosynthesis, soil, and soil respiration as the other scenarios, but again displays the trend of initial rapid increases or decreases followed by the leveling out of these flows and reservoirs.

Isotopic indicators are particularly important for the comparison of current climate changes to those of the past. Terrestrial isotopes across the scenarios indicated negative isotope excursions. The rate of changes in these isotopes mirrors the patterns of change in carbon reservoirs and processes determined by the scenarios. This result is expected, because the negative isotope excursion is largely driven by the release of isotopically light CO₂. Scenario A creates the largest negative isotopic shift across reservoirs followed by Scenario D, Scenario B, and Scenario C. Scenarios B and D are significantly different in the isotopic excursions, indicating the importance of 1-2GtC/yr in a scenario on the isotopic signature. Atmospheric and terrestrial excursions are the same across scenarios, and are only slightly larger than the excursions found in pedogenic carbonates (Fig. 17). The diffusion process in the carbonate equation could potentially account for the discrepancy. The terrestrial isotope signature recorded in pedogenic carbonates is most applicable to comparisons with past geologic events, due to its lasting presence in paleosols. The isotope shifts also emphasize the effect of different amounts,
rates, and time spans of carbon emissions, indicating that moderate to high releases over a moderate period of time will cause the greatest changes.

Perhaps the most interesting discrepancy in isotopes is that seen between the ocean and the terrestrial reservoirs. While the pedogenic carbonates undergo isotope shifts of -2 to -7‰, the warm surface and deep ocean range from -4.5 to -7.5‰. The isotopic shift of the cold surface ocean more closely mirrors that of terrestrial reservoirs. This is not unexpected, because the warm surface ocean, being the site of most photosynthesis in the ocean would be more likely to record a different oceanic isotopic signature. Scenario C predicts very different reactions of the isotopic signature of the ocean from the terrestrial reservoirs, indicating a large initial negative excursion and recovery in the terrestrial reservoirs that does not exist in the ocean. The discrepancy in isotopes could be attributed to changes in the ocean circulation system and ultimately ocean-atmosphere exchange as a result of increased carbon and temperature that do not affect terrestrial processes.

These results shed some light on hypotheses about the PETM. This model supports the need for release of organic CO₂ in addition to methane to cause large, prolonged temperature changes like those observed during the PETM. The initial reaction of temperature and atmospheric carbon to emission scenarios was relatively small. If this carbon had then been removed from the atmosphere, like methane, temperature increases would have remained relatively small. It was only after a period of time with CO₂ in residence that changes on the scale of 5-10 degrees Celsius took place. Emissions on the order of Scenario A over that same period of time would be enough to cause the changes observed during the PETM, but increase temperature too fast to be an
entirely appropriate analog. The results of the model show that the amount of carbon emitted per year, and the length of time for which it is emitted are crucial in determining the effect of such emissions on global temperature. It is possible that several scenarios could be overlain at once creating the effect of both sustained CO$_2$ input (such as Scenario B or D) combined with a larger shorter release of carbon (such as Scenario C). This combination could create the effect seen in the PETM with rapid releases of methane, perhaps underlain by a longer, slower release of carbon.

The isotopic results of the model also indicate the release of CO$_2$ during the PETM. Though the discrepancy in the isotopes of the terrestrial and ocean records is not as great as that seen in the PETM (Fig. 1), it still points to the presence of fundamental changes in the ocean during CO$_2$ excursions that are not reflected terrestrially. The discrepancy between the ocean isotopes and those found in the pedogenic carbonates, which are often used as evidence of terrestrial isotopic signatures, is closer to discrepancy found during the PETM, and serves as another indicator of the presence of CO$_2$ release. CO$_2$ forcing alters the processes of ocean circulation and changes the equilibrium capacities of seawater creating cascading changes in the isotopic signature of the ocean. This discrepancy could account for the portion of isotopic discrepancies that cannot be attributed to humidity or land plant diversification during the PETM, and is a direct result of the release of organic carbon.

There are several improvements to both the study and the model that could be considered for future work in order to obtain results on a finer scale, which would yield more precise comparisons to past geologic climate changes. Additions to the actual model that added a more complex ocean, delineated between C$_3$ and C$_4$ plants, and
recorded precipitation and humidity would increase the predictive capacities of the model, and allow it to be compared more closely with the hypothesized events of the PETM. The model was also only run for 3000 years. Running each scenario for 10000 years or more would yield important answers to questions about returning to steady state, and which reservoirs become sinks for excess carbon. Additionally, the use of four very different scenarios did not allow close comparison across scenarios, and thus obscured which aspect of emissions is most important in predicting the rate and magnitude of temperature change, carbon cycle perturbation, and isotope excursions. Using scenarios that kept magnitude, rate, or time period of emissions constant would have facilitated more tight comparisons.

CONCLUSION

Anthropogenic carbon emissions cause significant perturbations of the global carbon cycle. The results of four scenarios show that the amount of carbon emitted, the rate at which it is emitted, and the amount of time for which it is emitted are crucial in determining the effect of emissions on the atmosphere, temperature change, and carbon isotopes. Moderately high emissions over a moderate period of time produced greater changes in carbon reservoirs, temperature change, and isotope excursions than prolonged moderate emissions, or rapid high emissions. 318 Gt C released over 400 years caused temperature increases of 9.3 degrees Celsius with pedogenic carbonate isotope excursions of -7‰. The changes in the atmosphere, temperature, terrestrial processes, oceanic and carbonate isotopic signatures during model simulations provide evidence that CO₂ was released during the PETM, and that methane releases alone did not cause this period of
global warming. Use of a more complex model and more scenarios would yield better comparisons to past events.

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Bice, D. M., 1997, Exploring the dynamics of earth systems: a guide to constructing and experimenting with computer models of Earth systems using STELLA.


APPENDIX 1: Steady State Model Equations

Atmosphere(t) = Atmosphere(t - dt) + (ffb + Soil_Respiration + Plant_Respiration + Litter_Respiration + Volcano - atm–coc_trans - Photosynthesis - woc–atm_transfer) * dt
INIT Atmosphere = 600  {Gt C -- 1 Gt=1e15 g -- from IPCC, 1994}

INFLOWS:
ffb = emissions
Soil_Respiration = soil_disruption+((28.4/INIT(Soil))*Soil*(1+(Tsens_sr*global_temp)))
Plant_Respiration = tree_burning+(Photosynthesis*(50/100))
Litter_Respiration = Litter*(21/INIT(Litter))*(1+(Tsens_sr*global_temp))
Volcano = .6

OUTFLOWS:
atm–coc_trans = Area_co*k_a_co*(pCO2_atm-pCO2_co) {after Walker and K&S and B&P, set to give a flux of 74 following S&S}
Photosynthesis = (Pmax*(pCO2_eff/(pCO2_eff+Khs)))*(1+(Tsens_p*global_temp))
woc–atm_transfer = Area_wo*k_a_co*(pCO2_atm-pCO2_wo)

Cold_Surf_Oc(t) = Cold_Surf_Oc(t - dt) + (atm–coc_trans + advection + Runoff_1 - downwelling - org_c_dep_co) * dt
INIT Cold_Surf_Oc = 352.543845  {Gt C -- 1 Gt=1e15 g -- modified K&S, 1994}

INFLOWS:
atm–coc_trans = Area_co*k_a_co*(pCO2_atm-pCO2_co) {after Walker and K&S and B&P, set to give a flux of 74 following S&S}
advection = 20*(Warm_Surf_Oc/INIT(Warm_Surf_Oc))
Runoff_1 = Litter*(.2/INIT(Litter))

OUTFLOWS:
downwelling = 90.2*(Cold_Surf_Oc/INIT(Cold_Surf_Oc))
org_c_dep_co = 4
deep_oc(t) = deep_oc(t - dt) + (downwelling + org_c_dep_co + org_c_dep_wo - deposition - upwelling) * dt
INIT deep_oc = 38000  {Gt C -- 1 Gt=1e15 g -- from Kwon & Schnoor, 1994}

INFLOWS:
downwelling = 90.2*(Cold_Surf_Oc/INIT(Cold_Surf_Oc))
org_c_dep_co = 4
org_c_dep_wo = 6

OUTFLOWS:
deposition = .6
upwelling = 99.6*(deep_oc/INIT(deep_oc))
Del_C13_Atmosphere(t) = Del_C13_Atmosphere(t - dt) + (Isotope_Change_Atm) * dt
INIT Del_C13_Atmosphere = 0.157

INFLOWS:
Isotope Change Atm =
(1/Atmosphere)*(Atm_CO_Change+Atm_WO_Change+(Plant_Respiration*(Del_C13_Land_Biota-Del_C13_Atm))+
(Soil_Respiration*(Del_C13_Soil-Del_C13_Atm))+(Litter_Respiration*(Del_C13_Litter-Del_C13_Atm))+
(ffb*(Del_C13_FFB-Del_C13_Atm))+(Volcano*(Del_C13_Volc-Del_C13_Atm))-
(Photosynthesis*(-25)))

Del_C13_Cold_Surf_Oc(t) = Del_C13_Cold_Surf_Oc(t - dt) + (Isotope_Change_CSO) * dt
INIT Del_C13_Cold_Surf_Oc = 1.345

INFLOWS:
Isotope_Change_CSO = (1/Cold_Surf_Oc)*(Runoff_1*(Del_C13_Litter-Del_C13_Cold_Surf_Oc)+adv*De_C13_Warm_Surf_Oc-
Del_C13_Cold_Surf_Oc)+CO_Atm_Change-downwelling*(Del_C13_Cold_Surf_Oc-
Del_C13_Cold_Surf_Oc)+org_c_dep_co*(Del_C13_Cold_Surf_Oc-32-
Del_C13_Cold_Surf_Oc))

Del_C13_Deep_Ocean(t) = Del_C13_Deep_Ocean(t - dt) + (Isotope_Change_DO) * dt
INIT Del_C13_Deep_Ocean = -1.485

INFLOWS:
Isotope_Change_DO = (1/deep_oc)*(downwelling*(Del_C13_Cold_Surf_Oc-
Del_C13_Deep_Ocean)+org_c_dep_co*(Del_C13_Cold_Surf_Oc-32-
Del_C13_Deep_Ocean)+org_c_dep_wo*(Del_C13_Warm_Surf_Oc-32-
Del_C13_Deep_Ocean)+deposition*(Del_C13_Deep_Ocean-Del_C13_Deep_Ocean)-
upwelling*(Del_C13_Deep_Ocean-Del_C13_Deep_Ocean))

Del_C13_Land_Biota(t) = Del_C13_Land_Biota(t - dt) + (Isotope_Change_LB) * dt
INIT Del_C13_Land_Biota = -24.84

INFLOWS:
Isotope_Change_LB = (1/Land_Biota)*(Photosynthesis*(Del_C13_Atm-25-
Del_C13_Land_Biota)-Litter_Fall*(Del_C13_Land_Biota-Del_C13_Land_Biota)-
Below_Ground*(Del_C13_Land_Biota-Del_C13_Land_Biota)-
Plant_Respiration*(Del_C13_Land_Biota-Del_C13_Land_Biota))

Del_C13_Litter(t) = Del_C13_Litter(t - dt) + (Isotope_Change_Litter) * dt
INIT Del_C13_Litter = -24.84

INFLOWS:
Isotope_Change_Litter = (1/Litter)*(Litter_Fall*(Del_C13_Land_Biota-
Del_C13_Litter)-Runoff_1*(Del_C13_Litter-Del_C13_Litter)-
Runoff_2*(Del_C13_Litter-Del_C13_Litter)-Litter_Respiration*(Del_C13_Litter-
Del_C13_Litter)-Burial*(Del_C13_Litter-Del_C13_Litter))

Del_C13_Soil(t) = Del_C13_Soil(t - dt) + (Isotope_Change_Soil) * dt
INIT Del_C13_Soil = -24.84

INFLOWS:
Isotope_Change_Soil = (1/Soil)*(Below_Ground*(Del_C13_Land_Biota-Del_C13_Soil)+Burial*(Del_C13_Litter-Del_C13_Soil)-Soil_Respiration*(Del_C13_Soil-Del_C13_Soil))
Del_C13_Warm_Surf_Oc(t) = Del_C13_Warm_Surf_Oc(t - dt) + (Isotope_Change_WSO) * dt
INIT Del_C13_Warm_Surf_Oc = 7.002

INFLOWS:
Isotope_Change_WSO = (1/Warm_Surf_Oc)*(upwelling*(Del_C13_Deep_Ocean-Del_C13_Warm_Surf_Oc)+Runoff_2*(Del_C13_Litter-Del_C13_Warm_Surf_Oc)+WO_Atm_Change-org_c_dep_wo*(Del_C13_Warm_Surf_Oc-32-Del_C13_Warm_Surf_Oc)-advection*(Del_C13_Warm_Surf_Oc-Del_C13_Warm_Surf_Oc))
Land_Biota(t) = Land_Biota(t - dt) + (Photosynthesis - Below_Ground -Plant_Respiration - Litter_Fall) * dt
INIT Land_Biota = 610 \{610 Gt C -- 1 Gt=1e15 g -- from IPCC, 1994\}

INFLOWS:
Photosynthesis = (Pmax*(pCO2_eff/(pCO2_eff+Khs)))*(1+(Tsens_p*global_temp))
OUTFLOWS:
Below_Ground = Land_Biota*(25/INIT(Land_Biota))
Plant_Respiration = tree_burning+(Photosynthesis*(50/100))
Litter_Fall = Land_Biota*(25/INIT(Land_Biota))
Litter(t) = Litter(t - dt) + (Litter_Fall - Burial - Litter_Respiration - Runoff_2 - Runoff_1) * dt
INIT Litter = 80

INFLOWS:
Litter_Fall = Land_Biota*(25/INIT(Land_Biota))
OUTFLOWS:
Burial = Litter*(3.4/80)
Litter_Respiration = Litter*(21/INIT(Litter))*(1+(Tsens_sr*global_temp))
Runoff_2 = Litter*(.4/INIT(Litter))
Runoff_1 = Litter*(.2/INIT(Litter))
Soil(t) = Soil(t - dt) + (Below_Ground + Burial - Soil_Respiration) * dt
INIT Soil = 1500

INFLOWS:
Below_Ground = Land_Biota*(25/INIT(Land_Biota))
Burial = Litter*(3.4/80)
OUTFLOWS:
Soil_Respiration = soil_disruption+((28.4/INIT(Soil))*Soil*(1+(Tsens_sr*global_temp)))
Warm_Surf_Oc(t) = Warm_Surf_Oc(t - dt) + (upwelling + woc-atm_transfer + Runoff_2 - org_c_dep_wo - advection) * dt
INIT Warm_Surf_Oc = 616.549625 \{Gt C -- 1 Gt=1e15 g -- from K&S, 1994\}
INFLOWS:
upwelling = 99.6*(deep_oc/INIT(deep_oc))
woc–atm_transfer = Area_wo*k_a_co*(pCO2_atm-pCO2_wo)
Runoff_2 = Litter*(.4/INIT(Litter))

OUTFLOWS:
org_c_dep_wo = 6
advection = 20*(Warm_Surf_Oc/INIT(Warm_Surf_Oc))
Alk_co = 2.24 \{modified from K&S\}
Alk_wo = 2.27
Area_co = 1/3 \{fractional area\}
Area_wo = 2/3 \{fractional area\}
Atm_CO_Change = IF(atm–coc_trans>0)THEN-atm–coc_trans*CO_Atm_Shift ELSE - atm–coc_trans*(Del_C13_Cold_Surf_Oc+CO_Atm_Shift-Del_C13_Atmosphere)
Atm_WO_Change = IF(woc–atm_transfer>0)THEN -woc–atm_transfer*WO_Atm_Shift ELSE -woc–atm_transfer*(Del_C13_Warm_Surf_Oc+WO_Atm_Shift- Del_C13_Atmosphere)
CO3_co = Alk_co-C_conc_co
CO3_wo = Alk_wo-C_conc_wo
CO_Atm_Change = IF(atm–coc_trans>0)THEN atm–coc_trans*(Del_C13_Atmosphere+CO_Atm_Shift-Del_C13_Cold_Surf_Oc) ELSE atm–coc_trans*CO_Atm_Shift
CO_Atm_Shift = IF(atm–coc_trans>0)THEN(-2)ELSE(-9)
C_conc_co = (Cold_Surf_Oc/12000)/Vol_co \{1e18 moles/m^3\}
C_conc_wo = (Warm_Surf_Oc/12000)/Vol_wo \{1e18 moles/m^3\}
del_atm = (Atmosphere-600)-(DELAY(Atmosphere,1)-600)
Del_C13_FFB = -23
Del_C13_Volc = -6
del_deep_ocean = (deep_oc-INIT(deep_oc))-(DELAY(deep_oc, 1)-INIT(deep_oc))
del_land_biota = Land_Biota_Change-DELAY(Land_Biota_Change, 1)
del_surf_ocean = surf_ocean_chg-DELAY(surf_ocean_chg,1)
DS_D13 = 1.0044
global_temp = (pCO2_atm-280)*.01 \{°C relative to pre-industrial temp of 15; this relationship was determined from K&S, 1994\}
HCO3_co = (2*C_conc_co)-Alk_co
HCO3_wo = (2*C_conc_wo)-Alk_wo
KCO2_co = .035+.0019*(T_co-278)
KCO2_wo = .035+.0019*(T_wo-278)
Khs = 62.5
k_a_co = .278 \{Gt C/ yr ppm -- the observationally-derived rate constant\}
Land_Biota_Change = Land_Biota-INIT(Land_Biota)
pCO2_atm = Atmosphere*(280/600)
pCO2_co = 350*KCO2_co*(HCO3_co^2/C03_co)
\{this is from Walker's book, slightly modified\}
pCO2_eff = pCO2_atm-pCO2_min
pCO2_min = 30 \{ppm -- no photosynthesis can occur below this level\}
\[ p_{\text{CO}_2\_wo} = 350 K_{\text{CO}_2\_wo} \cdot (H_{\text{CO}_3\_wo}^2/C_{\text{O}_3\_wo}) \{\text{this is from Walker's book, slightly modified}\} \]

\[ \text{Pedogenic}_{\text{Del}\_C_{13}\_Hi} = \frac{1}{R_{\text{PDDB}}} \cdot (S_{\text{PCO}_2\_A_{\text{PCO}_2}\_Hi} \cdot D_{\text{S}_{13}} \cdot X_{\text{Del}\_C_{13}\_Soil} + p_{\text{CO}_2\_atm}) \cdot X_{\text{Del}\_C_{13}\_Atmo})}{(S_{\text{PCO}_2\_A_{\text{PCO}_2}\_Hi} \cdot (1 - D_{\text{S}_{13}} \cdot X_{\text{Del}\_C_{13}\_Soil}) + p_{\text{CO}_2\_atm} \cdot (1 - X_{\text{Del}\_C_{13}\_Atmo})) - 1) \cdot 1000 + 9.7 \]

\[ \text{Pedogenic}_{\text{Del}\_C_{13}\_Lo} = \frac{1}{R_{\text{PDDB}}} \cdot (S_{\text{PCO}_2\_A_{\text{PCO}_2}\_Lo} \cdot D_{\text{S}_{13}} \cdot X_{\text{Del}\_C_{13}\_Soil} + p_{\text{CO}_2\_atm} \cdot X_{\text{Del}\_C_{13}\_Atmo})}{(S_{\text{PCO}_2\_A_{\text{PCO}_2}\_Lo} \cdot (1 - D_{\text{S}_{13}} \cdot X_{\text{Del}\_C_{13}\_Soil}) + p_{\text{CO}_2\_atm} \cdot (1 - X_{\text{Del}\_C_{13}\_Atmo})) - 1) \cdot 1000 + 9.7 \]

\[ P_{\text{max}} = ((K_{hs} + 250) \cdot 100)/250 \]

\[ R_{\text{PDDB}} = 0.0112372 \]

\[ \text{soil\_disruption} = (\text{land\_use\_changes-tree\_burning}) \]

\[ S_{\text{PCO}_2\_A_{\text{PCO}_2}\_Hi} = 10000 \]

\[ S_{\text{PCO}_2\_A_{\text{PCO}_2}\_Lo} = 5000 \]

\[ \text{surf\_ocean\_chg} = (\text{Cold\_Surf\_Oc} + \text{Warm\_Surf\_Oc}) - (\text{INIT(Warm\_Surf\_Oc)} + \text{INIT(Cold\_Surf\_Oc)}) \]

\[ \text{tree\_burning} = \text{land\_use\_changes} \cdot 0.75 \]

\[ T_{\text{sens\_p}} = 0.04 \]

\[ T_{\text{sens\_sr}} = 0.1 \]

\[ T_{\text{co}} = 281 \quad ^{\circ}\text{K from K\&S} \]

\[ T_{\text{wo}} = 298 \quad ^{\circ}\text{K} \]

\[ V_{\text{ol\_co}} = 0.0121 \quad \{1E18 \text{ m}^3 \text{ this is the upper 150 m}\} \]

\[ V_{\text{ol\_wo}} = 0.0242 \quad \{1E18 \text{ m}^3 \text{ this is the upper 100 m}\} \]

\[ W_{\text{O\_Atm\_Change}} = \text{IF}(w_{\text{o\_atm\_transfer}>0) \text{THEN}\ w_{\text{o\_atm\_transfer}} \cdot (\text{Del\_C_{13}\_Atmosphere} + W_{\text{O\_Atm\_Shift}} - \text{Del\_C_{13}\_Warm\_Surf\_Oc}) \text{ELSE}\ w_{\text{o\_atm\_transfer}} \cdot W_{\text{O\_Atm\_Shift}} \]

\[ W_{\text{O\_Atm\_Shift}} = \text{IF}(w_{\text{o\_atm\_transfer}>0) \text{THEN}(-2) \text{ELSE}(-9) \]

\[ X_{\text{Del\_C_{13}\_Atmo}} = R_{\text{PDDB}} \cdot (\text{Del\_C_{13}\_Atmosphere}/1000 + 1) / (1 + R_{\text{PDDB}} \cdot (\text{Del\_C_{13}\_Atmosphere}/1000 + 1)) \]

\[ X_{\text{Del\_C_{13}\_Soil}} = R_{\text{PDDB}} \cdot (\text{Del\_C_{13}\_Soil}/1000 + 1) / (1 + R_{\text{PDDB}} \cdot (\text{Del\_C_{13}\_Soil}/1000 + 1)) \]

\[ \text{emissions} = \text{GRAPH}(\text{time}) \]

\[ (0.00, 0.00), (10.0, 0.00), (20.0, 0.00), (30.0, 0.00), (40.0, 0.00), (50.0, 0.00), (60.0, 0.00), (70.0, 0.00), (80.0, 0.00), (90.0, 0.00), (100.0, 0.00), (110.0, 0.00), (120.0, 0.00), (130.0, 0.00), (140.0, 0.00), (150.0, 0.00), (160.0, 0.00), (170.0, 0.00), (180.0, 0.00), (190.0, 0.00), (200.0, 0.00) \]

\[ \text{land\_use\_changes} = \text{GRAPH}(\text{time}) \]

\[ (0.00, 0.00), (10.0, 0.00), (20.0, 0.00), (30.0, 0.00), (40.0, 0.00), (50.0, 0.00), (60.0, 0.00), (70.0, 0.00), (80.0, 0.00), (90.0, 0.00), (100.0, 0.00), (110.0, 0.00), (120.0, 0.00), (130.0, 0.00), (140.0, 0.00), (150.0, 0.00), (160.0, 0.00), (170.0, 0.00), (180.0, 0.00), (190.0, 0.00), (200.0, 0.00) \]
APPENDIX 2.
Global carbon cycle model reservoirs, fluxes, and convertors. Reservoirs units are GtC, fluxes are given in GtC/yr. Black arrows indicate origin and destination of principle flows, black circles with pink outline indicate the primary processes determining the magnitude of these flows. Pink arrows indicate the connections between reservoirs, convertors, and processes necessary to the equations. Black open circles are convertors.