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**THE
GLOBAL
CARBON
CYCLE**

David
Archer

PRINCETON
PRIMERS IN
CLIMATE

THE GLOBAL CARBON CYCLE

Princeton Primers in Climate

David Archer, *The Global Carbon Cycle*

THE GLOBAL CARBON CYCLE

David Archer

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THE GLOBAL CARBON CYCLE

1 CARBON ON EARTH

A TOUCH OF MAGIC

The carbon cycle of the Earth differs from the other topics covered in the Princeton Primer series on the Climate of the Earth in that it is alive. Hurricanes, El Niño, and radiation in the atmosphere are all topics that one could spend a satisfying lifetime studying, but living matter somehow transcends the reductionist physical sciences that capture those other phenomena so well.

The second law of thermodynamics states that the universe runs downhill from order to disorder. Even in a universe with life in it, the principle of entropy—the drive from order to disorder—holds. But within such a universe, subject to the second law of thermodynamics, life creates for itself pockets of the most exquisite order and stability. It does so by creating even greater disorder in its surroundings, thereby adhering to the letter of the second law while giving the impression of somehow flouting it.

Living systems are able to create pockets of stability in part because they are immensely complicated. Birds and bees and flowers and trees are physical-chemical machines more intricate than any created by the human intellect. Chemical concentrations are altered using

enzymes, each a chemical catalyst specifically tuned to its function, its activity regulated by means of other chemical signals. The whole machine can be replicated from a few molecular tools and the information coded in DNA. The machine works with such accuracy and subtlety that a boy can grow up to look like his father.

Another characteristic of life on Earth is that it seems to possess an intrinsic stability. Fossil carbon energy production and carbon dioxide (CO_2) release take place in the context of three grand stabilizing feedback systems in the global biosphere carbon cycle: the weathering CO_2 thermostat, the oxygen homeostat, and the ocean's calcium carbonate pH-stat.

Carbon Dioxide

Earth's climate has navigated a path that stayed within a narrow range, the freezing and boiling points of water, since the very first sedimentary rocks appeared, shortly after the birth of the Earth. Meanwhile, the heat source for the surface of the Earth, the sun, has gotten 25% brighter over geologic time. This "faint young sun paradox" was first noted by the astronomer Carl Sagan (Sagan and Mullen 1972).

Part of the explanation has to do with the carbon cycle and a mechanism called the weathering CO_2 thermostat, which stabilizes Earth's climate by regulating the CO_2 concentration in the atmosphere (see chapter 2). The idea is that the rate of chemical weathering, which results in carbon sequestration as calcium carbonate

Box 1.1

Units of the Carbon Cycle

The science of the carbon cycle is fraught with unit wars, analogous to metric versus English units at the grocery store or the gas station. One learns one's way around in one set of units, and information presented in other units has to be translated to understand it. If a car gets 60 kilometers per liter of gas, is that good? I have to convert it to miles per gallon to compare it with what I know. It is the same way with units in the carbon cycle. In this book I use the most common units, gigatons of carbon, or Gton C. The prefix *giga-* means 10^9 , so a gigaton is a billion metric tons. A metric ton is equal to 10^6 grams, so $1 \text{ Gton C} = 10^{15} \text{ g C}$.

A chemist will tell you that it is more convenient to count atoms than to weigh them. Carbon dioxide is composed of carbon and oxygen atoms in a ratio of 1:2—in atoms, not grams. Chemists count atoms using the unit of mole, where a mole is a number of atoms that will give you the atomic weight of the element in grams. There are 6.02×10^{23} atoms or molecules in a mole, and mass of a mole of molecules, in grams, is equal to the sum of the atomic masses of the elements. One mole of carbon (12 g) will react with two moles of oxygen (twice 16 g) to make one mole of CO_2 (44 g).

One can convert units by writing them out explicitly and canceling them using conversion factors:

$$1 \text{ Gton C} \times (10^{15} \text{ g/Gton}) \times (\text{mol C}/12 \text{ g}) = 8.3 \times 10^{12} \text{ moles},$$

where the 12 grams in the second factor is the molecular weight of carbon (but only roughly, since there is also some carbon-13 and carbon-14 in natural carbon; see box 2.3, “The World According to Carbon Isotopes”).

The disadvantage of using mass units is exemplified by the potential for confusion in the climate literature between the

(Box 1.1 continued)

mass of carbon alone and the mass of CO₂, including the oxygen atoms. Some people talk about the costs of reducing CO₂ emissions in dollars per ton of carbon, others in dollars per ton of CO₂; the units are very different. The conversion is

$$1 \text{ g C} \times (44 \text{ g CO}_2 / 12 \text{ g C}) = 3.7 \text{ g CO}_2,$$

where 44 g is the approximate mass of a mole of CO₂.

I think of the conversion factor as equivalent to the statement that 44 g CO₂ is equal or somehow equivalent to 12 g C. They are different units but equivalent, in the way that 2.54 cm is equivalent to 1 inch. A fraction such as 44 g CO₂/12 g C, where the numerator equals the denominator conceptually, divides out to a value of one. You can multiply a number such as 1 g C by the number one, in whatever form, without changing the magnitude of the number, only its units.

(CaCO₃) in sedimentary rocks, increases as a function of temperature, pulling the CO₂ concentration down if the Earth is too warm or allowing it to build up if the Earth is too cold. Unfortunately for the global warming climate event, it will take hundreds of thousands of years for the thermostat to restore Earth's climate to its natural carbon-cycle balance (Archer 2009).

Oxygen

The biosphere captures energy from sunlight and stores it in chemical form, maintaining a huge chemical disequilibrium in the biosphere that would not exist on a lifeless planet. This is another example of a second-law-flouting

Box 1.2**Reservoirs of Carbon**

CO₂ is a trace constituent in the atmosphere, comprising only about 0.039% of all the gas molecules (which works out to 390 ppm, or parts per million). If all the CO₂ in the atmosphere were to solidify into dry ice, the snowfall would be only about 10 cm deep. The atmosphere currently contains about 780 Gton C. A handy conversion factor is that 1 Gton C in our atmosphere changes the concentration of CO₂ by about 0.5 ppm.

The atmosphere acts as a kind of Grand Central Station with respect to the carbon cycle, and the other reservoirs interact with each other primarily by trading carbon through the atmosphere, even though the atmosphere holds only a tiny fraction of Earth's carbon. The situation is different on Venus, for most of that planet's carbon is found in its atmosphere. The difference between the two planets is liquid water, which enables weathering chemical reactions to take place on Earth. Venus lost its water early on. Water is an essential component of the climate-stabilizing weathering CO₂ thermostat mechanism. On Venus, the thermostat is broken.

The land biosphere is the most visible part of the carbon cycle to us, and it holds much more carbon than the ocean biosphere does (trees are much larger than single-celled plankton). The land surface stores carbon in organic form in living things and even more abundantly as the organic carbon remains of plants in soils. Grasslands accumulate a lot of organic carbon in their soils, so that the total amount of carbon per acre is about equal to that in forests, even though the carbon is more obvious in the forests. There is about as much living carbon on land as there is atmospheric carbon, perhaps 500 Gton C.

The amount of carbon attributed to the soil pool depends on how deep the boundary is between soil and the geologic

(Box 1.2 continued)

record, where soils might be affected by changes in climate but the carbon below that is out of reach. The usual soil depth is assumed to be one meter, resulting in a soil carbon pool of about 1,500 Gton C as soil carbon, twice as much as is in the atmosphere.

The oceans contain about fifty times more carbon than the atmosphere does, about 38,000 Gton C. Most of the carbon in the ocean is in the inorganic forms: dissolved CO_2 , carbonic acid (H_2CO_3), bicarbonate ion (HCO_3^-), and carbonate ion (CO_3^{2-}). These chemical forms of carbon are oxidized, just as CO_2 is oxidized, rather than being chemically “reduced,” as organic carbon is. This means that it doesn’t take photosynthetic energy to convert carbon from one of the inorganic forms to another; it merely takes a change in the pH, the acidity of the water. Most of the carbon is in the pH-neutral form of bicarbonate, and the concentrations of the other species depend on the pH of the seawater.

Sedimentary rocks contain most of the Earth’s carbon, in chemical forms of limestone (CaCO_3) and organic carbon, mostly in the form of a random indescribable goo called kero-gen. The sediments were originally deposited in water but are now found over most of the surface of the Earth, including the highest mountaintops.

Fossil fuels make up only a small fraction of the buried organic carbon in the Earth, but even so, there is enough carbon to knock the carbon cycle significantly out of whack. Fossil fuel combustion takes carbon that was sleeping in sedimentary rocks and injects it into the atmosphere. Most of the fossil carbon is coal, and of that there is enough to increase the CO_2 concentration of the atmosphere to about ten times its natural concentration, if it were all released at the same time.

For further information, consult chapter 7 in Denman et al. 2006.

local pocket of order generated by living things. In the 1970s, the geochemist James Lovelock wrote that the chemistry of the biosphere is charged up like a battery and we are machines running off that battery, one pole connected to the oxygen in the atmosphere and the other pole connected to food, the organic carbon produced by photosynthesis (Lovelock 1974).

The oxygen content in the atmosphere, essentially a measure of how “charged up” the battery of the biosphere is, also seems to be stabilized by the processes going on in the biosphere. Since the advent of multicellular life forms that leave fossils, 600 million years ago, the air has had about as much oxygen as it has today, occasionally a bit more or less. If oxygen dropped to one-tenth of its present-day concentration, multicellular life would end and the fossils would disappear. And if the oxygen concentration ever increased to ten times its present value, wet wood would burn, and a spark of lightning would ignite an unstoppable fire. Neither of these disasters seems to have happened in Earth’s history (Berner 2004).

Oxygen is produced by photosynthesis, the process that also produces the organic matter in our food and in fossil fuels. Most of the organic carbon from plants decomposes eventually, and when it does, it consumes the same amount of oxygen as was produced by photosynthesis. The only way oxygen can be left over to build up in the atmosphere is when the organic carbon escapes degradation by being buried someplace where nothing eats it. The oxygen homeostat is not as clearly understood as the CO₂ thermostat,

Box 1.3**Oxidation and Reduction of Carbon**

Oxidation and reduction (abbreviated “redox”) reactions change the number of electrons possessed by the atoms in the reaction. Here we are concerned with carbon atoms in particular, but many other elements undergo changes in oxidation state, such as oxygen, nitrogen, and iron.

In the bookkeeping of electrons, the difference between the carbon atoms in CO_2 and methane (CH_4) is in the carbon atoms’ chemical partners. Oxygen is greedy for two of carbon’s electrons, which are shared with oxygen in a double bond. When oxygen is combined with carbon, the bookkeeping practice is to assign the carbon a deficit of two electrons. Since each electron has a charge of -1 , the carbon atom has a bookkeeping charge of $+2$, one for each electron. The carbon in CO_2 has two oxygen partners, each taking two electrons, leaving the carbon with an oxidation state of $+4$.

In methane, hydrogen donates one electron each to its chemical partners. The carbon atom in methane has an oxidation state of -4 , a negative charge for each electron coming from each of four hydrogens.

A carbon with a positive oxidation state is called oxidized, consistent with the oxygens that make up the CO_2 molecule. When the oxidation state is negative, it is called “reduced,” consistent with the lower number of the oxidation state. Chemists call carbon “organic” when it is at least partially reduced, as a historical holdover from the early association of reduced carbon with life. Note the contrast with everyday usage: a chemist would call the pesticide DDT a form of organic carbon, but a grocer uses the word to mean that food is grown without using pesticides like DDT.

The organic matter produced when plants grow is complex stuff (see box 1.5, “Biochemistry 101”), but on average, the carbon atoms have an oxidation state of about zero, similar to a molecule of CH_2O .

but it probably has to do with the effect of oxygen in the ocean on organic carbon burial (see chapter 3).

Ocean pH

The acidity, or pH, of the ocean is also controlled by elements of the carbon cycle, in particular the cycling of CaCO_3 between sedimentary rocks and the ocean (Broecker and Takahashi 1978). CaCO_3 , the chemical constituent of limestone, a very common kind of sedimentary rock, behaves chemically as a base and dissolves in acid. The pH of the ocean is controlled by the dissolved CaCO_3 that flows into and out of the ocean. The input is from the dissolution of land rocks, including CaCO_3 -containing rocks, a geochemical reaction weathering, and the output is in the form of CaCO_3 deposition on the seafloor. The ocean pH must be right for sedimentation to balance weathering, and as the ocean balances its CaCO_3 budget, it controls the ocean pH. This mechanism, called the CaCO_3 pH-stat, takes a few thousand years to adjust the ocean's pH, faster than either the weathering CO_2 thermostat (100,000 years) or the oxygen homeostat (2 million years) (see chapter 4).

THE MOODS OF THE CARBON CYCLE

To say that the carbon cycle is highly nonlinear is an understatement; we might even think of it as quirky. In some instances and on some time scales, the carbon cycle acts as a stabilizing influence on climate, a negative feedback. This is true today, for example: the oceans and some component of the land surface are removing CO_2 from the atmosphere at a significant rate, reducing the climate impact of our releasing that CO_2 . In other cases, on different time scales and with different web diagrams of cause and effect, the carbon cycle can be an amplifier of climate variability, as for instance a co-conspirator in the ice age climate cycles that have been changing the face of the Earth for the last 2 million years.

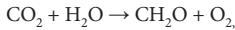
The Stable Geologic Carbon Cycle

On time scales of a million years and longer, the weathering CO_2 thermostat mechanism regulates the atmospheric CO_2 concentration and the climate of the Earth. The components of the thermostat are chemical weathering—essentially the dissolution of rocks into freshwater on land—and CO_2 degassing from the Earth in volcanic gases and deep-sea hydrothermal vent fluids (Walker, Hays, and Kasting 1981).

The set-point of the CO_2 thermostat can be tweaked, like changing the target temperature of a house's thermostat. Any change in the processes of chemical weathering or CO_2 degassing can alter the set-point of the

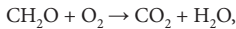
Box 1.4**Photosynthesis and Respiration**

The biosphere is energized by sunlight, which is captured and converted to chemical energy by the process of photosynthesis. The chemical reaction for most photosynthesis on Earth is



where CH_2O is a very approximate chemical formula for organic carbon, the chemical form of life.

In an oxic atmosphere, it takes energy to reduce carbon, and the energy is captured from sunlight by the photosynthetic machinery. This chemical energy can be harvested by running the photosynthesis reaction in reverse:



in a process called respiration. Respiration, essentially a combustion reaction, provides the fuel for the metabolism of all living things. Fossil fuels are simply buried organic carbon from past photosynthesis, and we extract energy from it by means of chemistry very similar to biological respiration.

thermostat. Mountain uplift makes bedrock dissolve faster by shedding soils and exposing them to erosion. Plants pump CO_2 down into soil gases, which drives the rocks chemically to dissolve. If the continents of the Earth happen to drift into the tropics, they will dissolve more quickly because there is more rainfall in the tropics. Making it easier to do chemical weathering depletes the atmosphere of CO_2 , cooling the planet until the rate

of chemical weathering falls back into balance with CO_2 degassing from the Earth.

If the rate of CO_2 emission from the Earth were higher at some point in the past, it would have pushed atmospheric CO_2 to a higher concentration and the Earth to a warmer climate, until the weathering rate was high enough to balance the higher rate of CO_2 degassing. These are the processes invoked to explain the slow shifts in Earth's climate from the hothouse climates of 50 million years ago to the icy climates such as today's.

The Unstable Ice Age Carbon Cycle

For the last several million years, ice sheets and glaciers around the world, and particularly in North America and northern Europe, have grown and melted back in a complex rhythm with beats of tens and hundreds of thousands of years. The timing of the ice sheets' growing and collapsing coincides with the rhythm of variations in Earth's orbit around the sun. In particular, the ice seems to depend on the intensity of sunlight at about 65° North latitude, at around the summer solstice. When John Imbrie wrote his classic book *Ice Ages* in 1979, the story seemed all but solved (Imbrie and Imbrie 1979).

Then came measurements of the CO_2 concentration in bubbles of ancient atmosphere trapped in polar ice. The measurements showed that the CO_2 concentration in the atmosphere varies systematically in concert with the progression of the ice ages (Barnola et al. 1987). The carbon goes from the atmosphere into the ocean during

a glacial time, and the lowered CO_2 concentration in the atmosphere chills the planet down even more than it would cool from the ice sheets alone.

There is an understandable causal link between the orbit and the ice sheets, but no easy way to imagine the orbit causing the carbon cycle to change directly. So the carbon cycle seems to be acting as a positive feedback mechanism to the orbitally driven climate changes on this time scale. Ice sheets, global temperature, and the carbon cycle form a loop of cause and effect: perturb any one of these and the others will respond. The result over the glacial cycles is that the change in global temperature was about twice as strong because of the amplifying effect of the carbon cycle. Notice that the character of the carbon cycle has changed, from calming and stabilizing the climate of the Earth on million-year time scales to amplifying climate changes driven by wobbles in Earth's orbit on time scales of tens of thousands of years.

One explanation for the CO_2 cycles that would account for at least the direction of the response is based on the solubility of CO_2 in water. Cooler water can hold more CO_2 than warm water can, so when the Earth cools down, more CO_2 would dissolve in the cooler ocean. However, as will be described in detail in chapter 3, the CO_2 cycles are stronger than can be explained by this mechanism alone. In fact, it's not clear what drives the glacial CO_2 cycles.

The glacial cycles are shorter than the response time scale for the weathering CO_2 thermostat, so it is as if, in a house, an intermittent sunbeam coming in a window

Box 1.5**Biochemistry 101**

Living carbon is organized into distinct chemical classes of biomolecules. These are all constructed from carbon atoms that are somewhat reduced, so all are called organic carbon of various types (figure 1).

Carbohydrates are composed of sugar molecules, ring structures that generally have a chemical formula $(\text{CH}_2\text{O})_n$, such as glucose ($\text{C}_6\text{H}_{12}\text{O}_6$). The sugars can be joined together into dimers, such as sucrose, and longer chains, such as starches. Cellulose, despite its unappetizing feel to our palates, is also composed of sugars, but the sugars are joined by a chemical bond in a geometry which is like a lock that our toolkit of enzymes is unable to open. Hence, cellulose digestion is based on symbiosis with microorganisms, bacteria and archaea, that do possess the required enzyme.

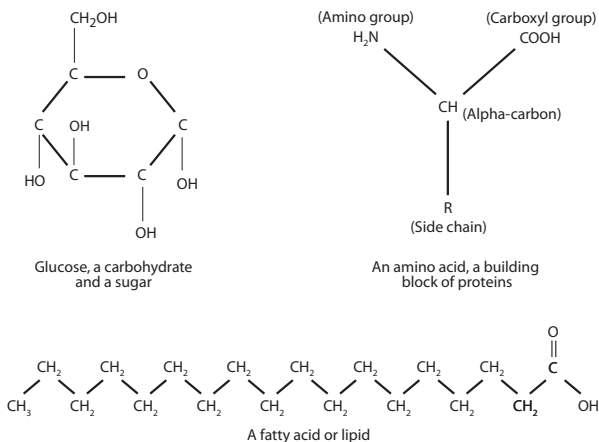


Figure 1. Biomolecules.

Proteins are chains of amino acids, each containing a backbone of a carbon atom joined to an amine group in one direction and a carboxylic acid group in the other ($\text{NH}_4^+ - \text{C} - \text{R} - \text{COO}^-$). There are twenty-six different amino acids, with different atoms or groups of atoms substituting for the R group. The amino acids can be put together like a Lego set to build chemical reaction machines called enzymes, as well as structural materials such as muscle fibers and collagen.

Lipids (fats) are chains of CH_2 groups and as such are more chemically reduced than carbohydrates in the intermediary redox state. They are also electrochemically less polar than carbohydrates, and tend to be less soluble in water for this reason (the word for this is “hydrophobic”). Biological lipids typically terminate with a slightly more polar end, making them more soluble in water (“hydrophilic”), and contain a few oxygen atoms. Lipids are used in cell walls, with the hydrophobic chains buried in the interior of the wall and the hydrophilic polar ends positioned at the boundary between the cell wall and the fluid on the inside and outside of the cell. The hydrophobic CH_2 chain, stripped of the hydrophilic end after the death of the cell, is the source of the oil and much of the natural gas in fossil fuel reserves.

Although the words *carbohydrates* and *hydrocarbons* look similar, they denote sugars and oils, respectively. These are very different types of molecules.

warms the place up a bit, then is blocked, allowing the house to cool faster than the furnace can control the temperature. The slow response time of the furnace and thermostat allows shorter deviations from the set-point temperature.

The funny thing about the carbon cycle is that the same carbon-cycle machinery both stabilizes the climate

(on million-year time scales) and perturbs it (on glacial cycle time scales), as if the carbon cycle were fighting with itself. It would be analogous to some erratic fault in the furnace, driving the house to warm up and cool down, while the thermostat tries to control the temperature of the house by regulating the furnace as best it can. Time to call the furnace guy!

THE CARBON CYCLE TODAY AND IN THE FUTURE

The multiple personalities of the carbon cycle in the past prompt the question, which carbon cycle are we dealing with now? Will we get the calming voice of restraint or the spiteful saboteur?

To the natural carbon cycle, human activity is adding a new flux of carbon from the solid Earth (fossil fuels) to the atmosphere. The carbon cycle today is helping us out by absorbing about half of our CO₂ emissions into the oceans and the land's surface. The carbon cycle is moderating the climate impacts of our CO₂ release, acting as a stabilizing negative feedback. In this regard the carbon cycle seems different in character from what it was through the glacial cycles, when it amplified climate change.

One difference between global warming and the glacial cycles is that climate today is driven by CO₂ input, while the glacial cycles were driven by changes in temperature from wobbles in the Earth's orbit. One possibility is that the carbon cycle could, in general, damp down

Box 1.6**Origins and Inventories of Fossil Fuels**

Coal is the most abundant fossil fuel, holding roughly fifty times more carbon than either of the other two forms of fossil fuel, oil and natural gas. The organic carbon in coal comes from plant material, mostly moss, deposited in standing-water swamps where it was protected from degradation by being cut off from the oxygen in the air. Peat from freshwater swamps tends to be cleaner than brackish or saltwater swamp remains because sea salt contains sulfate (SO_4^{2-}), which is reduced to sulfide (H_2S) in the anaerobic conditions of the swamp. Unless it is captured at the power plant, the sulfur winds up as the dominant source of acidity in acid rain. Sulfide deposits in coal also tend to be rich in mercury (Hg), making coal combustion the leading source of mercury in the environment.

Mature coal is essentially pure carbon. The hydrogen and oxygen that were originally associated with the carbon in the biomolecules were driven off by extended cooking in the subsurface Earth, at temperatures of ca. 300°C for tens of millions of years. With a chemical formula C_n , the oxidation state of the carbon in the coal is about zero. This is less reduced than oil ($\text{CH}_3(\text{CH}_2)_n\text{CH}_3$) or natural gas, which is mostly methane (CH_4). Because it involves the transfer of fewer electrons, the combustion of coal delivers less energy per carbon than from the combustion of other forms of fossil fuels.

Oil and most natural gas originate from the remains of microscopic algae in the ocean, the phytoplankton. Usually their organic carbon is deposited in very low abundance, diluted by other material such as CaCO_3 , silica (SiO_2), and clay minerals that originate on land. Under particular circumstances sediments can accumulate that contain much higher concentrations of organic carbon. Oil source rocks typically contain

(Box 1.6 continued)

3–10% organic carbon by weight, and they are relatively rare, typically only a few meters thick but extending long distances horizontally. Their upper and lower boundaries are sharp, indicating that some factor, such as the oxygen content of the water, changed suddenly to turn carbon preservation on or off.

Oil forms when the source rocks are cooked to the right temperature. If the stew is overcooked, the result is natural gas. The oil or gas, in order to be harvestable, has to migrate through pores or cracks in the solid Earth, collecting together in a trap that must also exist, preventing the fluids from migrating out of the solid Earth entirely. Because of the special circumstances required, there is much less oil and gas available to harvest than coal, and the distributions of both oil and gas are very spotty. Most of the world's oil is found in the Middle East, and about half of the world's natural gas. Most of the rest of the natural gas is in Russia.

Methane, as the most reduced form of carbon, delivers more energy per carbon atom than either oil or coal. Methane also burns more cleanly than coal, releasing fewer pollutants such as mercury, sulfur, and aerosols (droplets in the air).

Methane is expensive to transport long distances, so the price of natural gas varies a lot, depending on the distance of the consumer from the gas's origin. Gases expand to fill or escape their containers, unlike liquids and solids, which can be transported in unpressurized tankers. Natural gas can be either compressed (CNG), usually in cylinders that look like scuba tanks, or liquid natural gas (LNG), which takes energy and serious equipment to produce from gas. The condensation temperature for methane (-161°C) is much lower than for its higher-C cousins, propane (-43°C) and butane (-0.6°C).

Methane is produced from organic carbon buried in sediments. Microorganisms called archaea, the most primitive form of life on Earth, produce methane as a by-product of

fermentation. Fermentation releases energy, which archaea use to drive their metabolisms. If the organic carbon is heated, methane can form spontaneously without any biological help (see box 5.3, “Methanogenesis Chemistry”).

Adding up the total inventories of the fossil fuels is a bit tricky because we’re interested in the total amount of each that might ultimately be recoverable, including finds yet to be made and fuels that cannot yet be extracted with currently available technology. There are also fuzzy definitions, especially of “oil,” which lead to much larger estimates of supply if we start to include less traditional forms such as oil shales and tar sands. With these caveats, the canonical assumption among carbon cycle modelers is that there is about 5,000 Gton C available as coal, and perhaps 200 Gton C each of oil and gas. An authoritative source, a bit dated, is Rogner 1997. Compare these with the carbon inventories in the natural carbon cycle in box 1.2, “Reservoirs of Carbon.”

The industry unit for oil is the barrel. Each barrel contains about 100 kg of carbon, or about 8,000 moles. The latest British Petroleum estimate for the amount of oil left in the ground is 1,258 billion barrels, which is about 125 Gton C.

Natural gas is sold in units of volume—cubic feet or cubic meters. Because a gas is compressible, the gas is specified to be at a “standard temperature and pressure” of 25°C and one atmosphere of pressure. Under these conditions, one mole of any gas takes up about 22.4 liters, which is 0.0224 cubic meters, or about 0.8 cubic feet.

The inventory of natural gas according to British Petroleum is 185 trillion cubic meters, which can be converted into Gton through the following equation:

$$\begin{aligned} 185 \times 10^{12} \text{ m}^3 &\times (1 \text{ mole C}/0.0224 \text{ m}^3) \times (12 \text{ g C}/\text{mole}) \times (\text{Gton}/10^{15} \text{ g}) \\ &= 100 \text{ Gton C as gas.} \end{aligned}$$

(Box 1.6 continued)

Natural gas is also tabulated in units of energy content, for example joules or BTU (British thermal units). A cubic foot contains about 1,030 BTU of energy. The current price of natural gas is a few dollars per million BTU. This can be converted to a value per cubic meter with the following equation:

$$(1,030 \text{ BTU/ft}^3) \times (\$2/10^6 \text{ BTU}) \times (35 \text{ ft}^3/\text{m}^3) = \$0.07/\text{m}^3.$$

A BTU is nearly equivalent to a kilojoule (the conversion factor is 1.06).

A dollar buys about 5×10^8 joules of energy in the form of natural gas. For comparison, the cost of petroleum is about \$3.00 per gallon in the United States, yielding about 5×10^7 joule per dollar, ten times more expensive. Coal is cheaper, yielding about 8×10^8 joules per dollar. The cost of electricity is about \$0.05 per kilowatt-hour, which can be converted to the same units to 7×10^7 joules/dollar, more expensive than raw coal or gas but about half the cost of gasoline.

CO₂ fluctuations but amplify temperature fluctuations. But in the long run, it seems likely that the carbon cycle will start acting as a positive feedback, as for example melting permafrost soils allow peat deposits to decompose. The carbon cycle will have begun to release CO₂ rather than absorbing it. The conclusion we come to is that the natural carbon cycle is a wild card, as large an uncertainty as that of our own CO₂ emissions.

2 THE STABLE GEOLOGIC CARBON CYCLE

On geologic time scales, the carbon cycle acts to stabilize the climate and the oxygen concentration of the Earth in mysterious and wondrous ways.

THE PROCESSES DESCRIBED IN THIS CHAPTER ARE probably irrelevant for political consideration of climate change on human time scales. The stabilizing mechanisms of the carbon cycle simply work too slowly to make much difference on the time scales of our lives, say the coming century to the year 2100. However, the irrelevance of the slow carbon cycle to the immediate future is an important point, since ultimately the global warming climate event will last for as long as it takes these slow processes to act. The geologic carbon cycle also sets the stage for carbon cycle gymnastics on faster, and perhaps more immediately relevant, time scales.

On geologic time scales, the carbon cycle has much to do with the eerie stability of conditions on the surface of the Earth. British geochemist James Lovelock writes that life on Earth functions as a single organism, able to regulate the conditions on Earth the way a person regulates

his internal temperature or chemical composition. “Homeostasis by and for the biosphere” was how he put it in the title of an early article (Lovelock 1974).

To some extent, Lovelock’s Gaia hypothesis is more a philosophical definition than a refutable scientific proposition. Lovelock looks for cooperation and mutual benefit in the tasks that organisms perform—for example, animals excreting nitrogen waste in a biologically available form (urea, NH_2CONH_2) rather than in an unusable form such as nitrogen gas. We know that organisms compete with each other, so a state of cooperation between organisms to complete their Gaian housekeeping chores would appear to be unstable to invasion by some selfish beast who would prefer to keep all of his metabolic energy for perpetuating his own kind.

Regardless of where one draws the boundaries between organisms in the biosphere or what one thinks about competition, the stability that Lovelock pointed to in the biosphere, the apparent homeostasis, is very real, and to the extent that we understand it, it is largely due to the working of the carbon cycle.

THE ATMOSPHERIC CO_2 THERMOSTAT

The carbon cycle controls and stabilizes the CO_2 concentration of the atmosphere, acting as a global thermostat. The mechanism is based on a chemical reaction called the Urey reaction (Urey 1952):



The first compound, CaSiO_3 , is the simplest possible chemical formula for igneous rocks. Most real rocks have other elements in them, such as aluminum and sodium, and much more complicated chemical formulas than CaSiO_3 . At the risk of offending the geologists of the world even more egregiously, the reaction could be stripped down further to the bare minimum,



by removing an SiO_2 from each side. The essential chemistry that creates the weathering CO_2 thermostat is still there, in the weathering of the CaO component of igneous rocks. Carbon is recruited from atmospheric CO_2 and ultimately winds up in the chemical form of CaCO_3 in sediments of the ocean. Chemical weathering acts as a carbon sink (the opposite of a source) and provides a pathway for carbon to exit the fast surface carbon cycle and return to the solid Earth.

The main idea behind the thermostat is that when the temperature of the Earth rises, it accelerates the hydrologic cycle (the amount of freshwater running off the continents) and therefore the rate of chemical weathering (Walker, Hays, and Kastin 1981). This effect is due to the higher vapor pressure of water in a warmer atmosphere than a cooler atmosphere. More water vapor generates more rain when it gets squeezed out of the air as it rises and cools. Runoff rates on Earth today are much higher in the tropics than in the cooler high latitudes (Holland 1978). Everything else being equal, the weathering carbon sink would be stronger on a warmer planet than a cooler one.

The carbon sink from chemical weathering is balanced in a steady state by a carbon source, emerging from the solid Earth in volcanic gases and hot spring fluids. The combination of independent source and concentration-dependent sink for CO_2 makes for a stable negative feedback system that ultimately controls the CO_2 concentration of the atmosphere. An imbalance in the carbon fluxes to and from the solid Earth causes the atmospheric CO_2 concentration to rise or fall. As the CO_2 concentration changes, it alters the hydrologic cycle, and through that, the rate of the carbon sink from weathering.

If the atmospheric CO_2 concentration were too high, for example, the carbon sink for weathering would consume more CO_2 than could be replenished by the volcanic carbon source, and the atmospheric CO_2 concentration would drop. The planet would cool, slowing the hydrologic cycle, decreasing the carbon sink from chemical weathering. Eventually, after a few hundred thousand years, the weathering sink would return to balance with the CO_2 source.

The weathering CO_2 thermostat is at least partly responsible for the stability of Earth's temperature through geologic time, even as the heat output of the sun gradually increases (Carl Sagan's faint young sun paradox). Geologists find sedimentary rocks from the very earliest days of the history of the Earth, indicating that the Earth's temperature has managed to stay within the boiling and freezing temperatures of water for this entire time (although there may be a temporary exception to this rule in the snowball Earth scenario, described below).

It's not clear that the weathering CO_2 thermostat can explain the entire span of Earth's history—the sun was so cool during the earliest days of Earth's history that some other greenhouse gas, perhaps methane or ammonia, might have been helping keep the Earth warm. But the CO_2 thermostat serves as a sufficient explanation of the stability, and the vagaries, of global climate for the Phanerozoic era, the time of formation of the fossil-bearing deposits from the last 600 million years into the present, about which we know a lot more than about earlier times.

The strongest evidence in support of a weathering CO_2 thermostat mechanism is the stability of the CO_2 concentration in the atmosphere through the last 800,000 years, for which we have ice core CO_2 data. If the CO_2 sources (volcanoes) and sinks (weathering) were out of balance by 10%, they could double the CO_2 concentration in the air in about 50,000 years. There are glacial/interglacial cycles in CO_2 concentration (see chapter 3), but there is no long-term trend upward or downward in the concentrations. On long time averages, the fluxes balance to much better than 10% (Zeebe 2008).

The Slowest Climate Changes

The weathering CO_2 thermostat tries to maintain the CO_2 concentration of the atmosphere, and the climate, at some set-point, but there are ways in which factors such as the placement of the continents on the Earth's surface and the creation of mountains by tectonic plate collisions can alter the set-point of the thermostat (Berner

2004). On time scales of tens and hundreds of millions of years, the temperature of the Earth drifts up and down, between icy worlds like today's, when the Earth sports large ice sheets at or near both poles, called icehouse climates, and hothouse times, when the Earth would have felt tropical all the way to the poles.

Mountains tend to accelerate the global rate of chemical weathering by exposing fresh igneous rock to chemical scouring by freshwater. When igneous rocks weather, not all of the atoms are soluble in water. Some recrystallize back out of solution, forming another class of mineral called clay minerals. Clay minerals tend to have more water in their chemical structure than igneous rock minerals do, and they are softer. The clays left behind form the basis for the soils that cover most of the land's surface. Soils impede weathering by limiting contact between the rocks and the water.

Uplift, driven by tectonic collisions, therefore accelerates the rate of chemical weathering. But in steady state, after the weathering CO_2 thermostat has had time to equilibrate, the total rate of CO_2 consumption by weathering on Earth needs to balance the rate of CO_2 emerging from the Earth in volcanoes and hot springs. The end result of uplift, then, is to pull the atmospheric CO_2 concentration to a lower value, cooling the planet. The increased "weatherability" of a planet with mountains on it will be compensated for by a cooler climate and lower atmospheric CO_2 concentration. One theory for a generally cooling climate of the Earth over the last tens of millions of years, since the last "hothouse" era, about 50

million years ago, is the uplift of the Himalayas, driven by the collision of the Indian and Asian tectonic plates.

There is more runoff in lower latitudes, so if by chance the continents of the Earth find themselves mostly in the low latitudes, it would tend to stimulate weathering and draw down atmospheric CO_2 . Flooding and exposure of the continents by fluctuating sea levels also affects weathering, because weathering happens only on land, not under the oceans. On million-year time scales, global sea levels seem to rise and fall by hundreds of meters, as reconstructed by the area of the continental crust that is covered in ocean water, the way the continental shelves ringing most land areas are covered today. It is not clear why or how sea level varies this much, but it could be driven by changes in the average density of ocean crust, driven perhaps by the rate of seafloor spreading, or it could be that there is enough water dissolved in the minerals of the mantle to affect sea level as the water flows in and out of the solid Earth.

Plants and trees have the capacity to change the weatherability of the land surface, and therefore the set-point of the CO_2 thermostat and the climate of the Earth. Plants take up CO_2 through their leaves and release most of it below the soil surface, raising the soil gas CO_2 concentration to many times higher than the atmospheric concentration.

Since CO_2 is on the left-hand, "reactant" side of the Urey reaction, higher CO_2 concentrations should push the equilibrium chemical reaction to the right, dissolving more igneous rock. Plants, by pumping CO_2 into the

soils, might thereby be accelerating the rate of chemical weathering. By stimulating the chemical weathering reaction, the conquest of the land surface by plants in the Silurian (ending about 416 million years ago) may have acted to cool the planet.

The rate of CO_2 degassing from the Earth is also likely to vary through time. Most of the carbon is assumed to be recycled, from sedimentary rocks that subducted and ultimately released their CO_2 in the reverse, left-to-right direction of the Urey reaction,



or in abbreviated form,



This transformation is called metamorphism because it takes place at temperatures at which the rocks begin to deform and change chemically into what are called metamorphic rocks. Marble, for example, is metamorphosed CaCO_3 .

About half of the CO_2 degassing today is in mid-ocean ridge vent fluids. These are the spreading centers where new ocean crust is formed, far from any subduction zones where carbon sinks into the mantle as CaCO_3 (Kerrick 2001). The intriguing fact of the matter is that very little CaCO_3 is being subducted today, relative to how fast it is accumulating on the global seafloor (Plank 1998). The Earth is so old that geologists tend to expect budgets of things like CaCO_3 on the seafloor to balance, to have found a steady state. At present, however, CaCO_3

is accumulating on the seafloor faster than it is disappearing by subduction. On a long enough time average, accumulation and subduction of CaCO_3 must balance, because there is only so much seafloor available to put CaCO_3 on. Therefore there must be times in Earth's history when more CaCO_3 sediments were subducting into the Earth than is happening now (Edmond 2003).

Subduction zones tend to be found in the deepest parts of the ocean, where the crust has cooled and become denser. The crust is floating in the viscous fluid of the mantle like a raft floating in water, and as it gets denser it sinks, making the ocean deeper. In today's world, there is more subduction in the Pacific than in the Atlantic, and the Pacific is also generally deeper than the Atlantic. CaCO_3 tends to deposit in shallower and mid-depth waters, because it tends to dissolve under the higher pressure in the deep ocean (see box 3.3, "The CaCO_3 Cycle"). The Atlantic has CaCO_3 -rich sediments, while there is less CaCO_3 in sediments of the Pacific Ocean.

So perhaps CaCO_3 tends not to subduct, in general, because it tends to ride on relatively buoyant ocean crust that tends to float better in the mantle. Perhaps it takes exceptional circumstances to drive CaCO_3 into a subduction zone. One such time was when India collided with Asia, squeezing the CaCO_3 -rich sediments of the shallow Tethys Sea off the face of the Earth. The resulting CO_2 flux into the atmosphere may have been the reason for the warm early Eocene climate (Edmond 2003).

It is a somewhat open question how much of the carbon in CaCO_3 getting pushed into a subduction zone

would find its way to the atmosphere and how much would sink into the deeper mantle. CO_2 is degassing merrily at the subduction zone off the Pacific coast of South America, one of the few places on Earth where carbonate sediments subduct into the Earth. It seems reasonable to assume that stronger CaCO_3 subduction, as occurred in the Tethys Sea, would release CO_2 to the atmosphere and warm the climate.

On the other hand, more than half of the CO_2 coming out of the Earth today comes from spreading centers, which are generally far from subduction zones (Kerrick 2001). It's not clear how long it takes carbon to get from a subduction zone to a spreading center, but it could be millions or even hundreds of millions of years. CaCO_3 is known to exist in the mantle, in a rock type called carbonatites. When ocean crust subsides, it carries its relatively cool temperatures down into the Earth, keeping the carbonatites relatively stable. At the other end of the line, when mantle material rises up to form new ocean crust, it carries the heat of the Earth's interior up close to the Earth's surface. In this hotter setting, CaCO_3 has a greater tendency to release CO_2 . Thus, some fraction of subducted CaCO_3 might reside in the Earth's interior for a ride through the slow mantle-convection lava lamp rather than recycling its carbon quickly back to CO_2 in the atmosphere.

It has been only recently (comparatively) that critters evolved that would deposit CaCO_3 on sediments of the deep ocean, onto deep ocean crust that is susceptible to subduction. For much of Earth's history, CaCO_3 was a

tool that only nearshore life forms made use of. Has the evolution of planktonic foraminifera (100 million years ago) and coccolithophorids (220 million years ago) altered the global carbon cycle by flushing carbon down the subduction zones (Volk 1989)?

There is a computer model of the geologic carbon cycle, developed over decades by Bob Berner, called Geocarb (Berner and Kothavala 2001; Berner, Lasaga, and Garrels 1983). The drivers that Geocarb is most sensitive to are the plant invasion of land in the Silurian; the rate of seafloor spreading, which controls sea level and CO₂ degassing; and tectonic effects such as mountain building and the geographic distribution of the continents. The Geocarb model predicts high CO₂ concentrations in eras of Earth's history that geologists know to be warm, and low CO₂ concentrations in glaciated times (figure 2).

There are no ice core CO₂ concentration measurements from millions of years ago. Estimates of past CO₂ concentrations from these times are based on more indirect, proxy data rather than on direct measurement (Royer 2006). One proxy CO₂ measurement is derived from the number of vents in the waxy seal, called stomata, on the bottoms of leaves. Plants and trees in the lab grow more stomata when the CO₂ pressure is lower because they need the extra exchange capacity. The penalty they pay is increased water loss through the same vents. Trees and plants on Earth today experience different pressures of CO₂ as the total atmospheric pressure decreases with altitude, and their different conditions are reflected in their numbers of stomata vents.

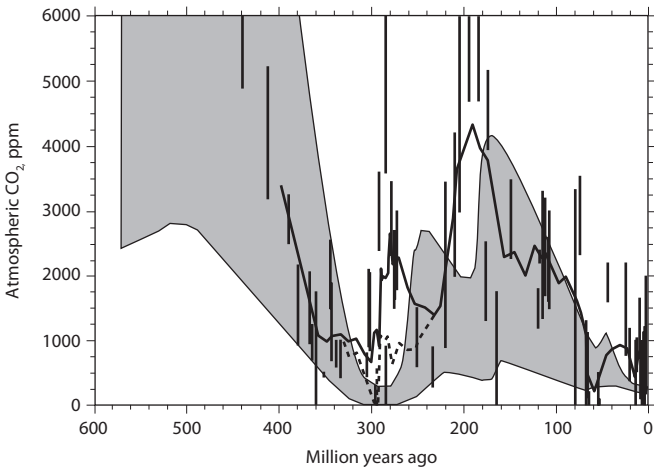


Figure 2. Model and proxy estimates of atmospheric CO₂ concentration in deep geologic time. (Source: Royer et al. 2001)

Stomatal-based estimates of CO₂ concentrations from millions of years ago may be affected by evolutionary changes as well as by environmental ones, but there are some very long-lived plant types that can provide very long records of stomatal-based CO₂ concentrations. For example, ginkgoes have existed in pretty much their current form for 270 million years.

Another proxy measurement is the carbon isotopic composition of CaCO₃ that forms in arid soils (see box 2.1, “Isotopes,” and box 2.3, “The World According to Carbon Isotopes”). The carbon in soil CaCO₃ comes from two sources, plants and the atmosphere. The carbon from plants is isotopically light, and that from CO₂ in the atmosphere is isotopically heavier. A rough atmospheric

Box 2.1**Isotopes**

An atom is classified as this element or that based on the number of positively charged particles in the nucleus. The positive charge number determines the number of electrons of the atom, and the electrons control the chemistry. But atoms can differ in the number of neutral particles, or neutrons, that they have in their nuclei. They are the same element (say, oxygen), with nearly the same chemistry, but they are different isotopes.

Much of what we know about the history and functioning of the biosphere comes from measurements of the relative abundances of different isotopes of elements (Faure 1977). This book mentions isotopic information from the elements carbon, oxygen, hydrogen, nitrogen, and silica. But the information we're looking for is encoded in extremely subtle variations in the proportions of the isotopic abundances. Rather than attempt to remember long numbers like 0.99762, for example (the fraction of oxygen that is oxygen-16), the patterns are expressed as deviations, as in "one sample is 2% lower in carbon-13 than another." This is called delta notation, and it is written as the lowercase Greek letter delta (δ). Because the variations are so small, the part per thousand (permil, sometimes written "per mil" or "per mille") is used rather than the part per hundred (percent). A part per thousand is written as ‰ by analogy to the percent sign, %. The formula for relating an isotopic concentration ratio to a δ value is

$$\delta = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1,000\text{‰}$$

by relating the sample to a standard, which must be carefully defined and agreed upon by the practitioners of the community. One of the carbon isotopic standards, a CaCO_3 rock called the Pee Dee Belemnite (PDB), has long since been used up; the

(Box 2.1 continued)

isotopic measurements are based on secondary standards that were once calibrated to the original PDB.

The nuclei of some isotopes are unstable, such as the radioactive carbon-14 used to measure the ages of things made of carbon like archaeological artifacts and geological samples (see box 2.3, “The World According to Carbon Isotopes”). Other isotopes are stable and do not decay. For stable isotopes, the strategy is to trace the signatures of processes that separate, or “fractionate,” the isotopes. Lighter isotopes tend to react faster than heavier ones. For example, water made of oxygen-16 evaporates slightly faster than water made of oxygen-18. The enzyme that captures CO_2 for photosynthesis has a slight preference for carbon-12 over carbon-13, so that carbon-12 reacts slightly faster. There can also be isotopic separation in equilibrium, such as a slightly lower vapor pressure for water with oxygen-18 versus oxygen-16.

CO_2 concentration estimate can be generated by asking how much atmospheric signature and how much plant signature it took to create the observed isotopic composition of soil CaCO_3 . Higher CO_2 concentration in the air would pull the carbon in soil CaCO_3 closer to the atmospheric isotopic composition.

Other proxies for atmospheric CO_2 have been constructed using isotopic measurements from sediment cores—the carbon isotopic compositions of particular biomolecules, for example—or the isotopic composition of boron atoms trapped in CaCO_3 . None of the available proxies for pre-ice core atmospheric CO_2 concentration are completely bullet-proof, but it is reassuring that most

Box 2.2**The World according to Oxygen Isotopes**

Oxygen atoms come in three stable sizes. Oxygen-16 is the most common, oxygen-18 is less abundant, and there is also a tiny fraction of oxygen-17 atoms. Variations in the relative abundances of the isotopes are expressed in the permil notation, $\delta^{18}\text{O}$, relative to one of several standards. One such standard for oxygen isotopes is called Standard Mean Ocean Water (SMOW). Another standard, used to compare oxygen isotopic values of CaCO_3 , is a particular fossil called the Pee Dee Belenite, or PDB.

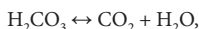
Oxygen isotopes of CaCO_3 on the seafloor provide a proxy measurement of changes in the amount of ice frozen into the great ice sheets. The hydrological cycle acts like a giant still for oxygen isotopes, refining the vapor in the air to remove the heavier isotope, oxygen-18. The oxygen isotopic composition of the ocean today is about 0‰ relative to SMOW (it should make sense to you that, relative to the ocean, the ocean is 0‰ different). The snow that falls on Antarctica has a $\delta^{18}\text{O}$ of about -50‰ .

During the Last Glacial Maximum, 18,000 years ago, there was enough water in the ice sheets to lower the global sea level by about 120 meters, removing about 2.5% of the volume of the ocean. Putting in or taking out 2.5% of an isotopic signal will dilute the signal by a factor of $1/2.5\%$, a factor of 40. Removing water at -50‰ to make an ice sheet leaves the ocean heavy by $50\text{‰}/40 = -1.25\text{‰}$.

The $\delta^{18}\text{O}$ composition of the ocean in the past is recorded in the isotopic composition of CaCO_3 . The oxygen in the CaCO_3 comes from a dissolved carbonate ion (CO_3^{2-}). The carbonate chemical family (H_2CO_3 , HCO_3^- , and CO_3^{2-}) all exchange oxygen atoms with each other as they interconvert by fast pH equilibrium chemistry (see box 3.1, "Carbonate System pH

(Box 2.2 continued)

Chemistry”). Carbonic acid exchanges oxygen rapidly with water via equilibrium with the dissolved gas:



anchoring the oxygen isotopic composition of HCO_3^- , $\text{CO}_3^{=}$, and CaCO_3 to the isotopic composition of the mother H_2O .

There is an offset between the isotopic composition of CaCO_3 in equilibrium with H_2O , depending on the temperature at which the CaCO_3 forms. This makes oxygen isotopic compositions in carbonates potentially useful as a paleothermometer.

The $\delta^{18}\text{O}$ of the source water can also be affected by evaporation of water, which tends to leave behind the heavier oxygen-18. Evaporation also changes the concentration of salt in the water left behind, so the evaporation effect is often referred to as a “local salinity effect” on the $\delta^{18}\text{O}$ of preserved CaCO_3 .

The $\delta^{18}\text{O}$ of CaCO_3 can be affected by both local temperature and salinity changes, and by changes in global ice volume. It takes additional information, different proxy measurements, to sort out how much each of these factors is driving a change in measured $\delta^{18}\text{O}$ values. Other proxy temperature measurement techniques include the magnesium concentration in CaCO_3 and various biomarkers. For the deep ocean during the glacial cycles, it appears that global ice volume and deep temperature changes each make about the same contribution to the $\delta^{18}\text{O}$ signal.

Further reading: Broecker and Oversby 1971.

of the available credible proxy techniques seem to give the same general answers about when CO_2 levels in the past were higher than today.

The time constant for the weathering CO_2 thermostat is on the order of hundreds of thousands of years. If the

rate of CO₂ degassing from Earth were to increase suddenly, changing the set-point of the CO₂ thermostat, it would take perhaps half a million years for CO₂ and the climate to fully respond to the change. The grand climate shifts between hothouse and icehouse in the geologic past generally took place on time scales much longer than the thermostat response time, drifting up and down over tens of millions of years. The pacing of these climate shifts is therefore set by the time scales of plate tectonics, the mountain building and soil formation, and changes in sea level and continental area, rather than by the response time of the weathering CO₂ thermostat mechanism.

Burps: PETM

In addition to ponderous drifts in climate, there are some abrupt burps in the geologic record. The clearest of these incidents happened 55 million years ago, at the boundary between the Paleocene and Eocene periods, called the Paleocene-Eocene Thermal Maximum, or PETM event (Kennett and Stott 1991). Documentation of the event comes from isotopes of carbon and oxygen preserved in CaCO₃ sediments from the deep sea (figure 3).

The carbon isotopic composition of the ocean reflects a balance between two sources, an isotopically light source which comes from decomposition of organic carbon, including the organic carbon in sedimentary rocks, and an isotopically heavy source, which comes from the

CHAPTER 2

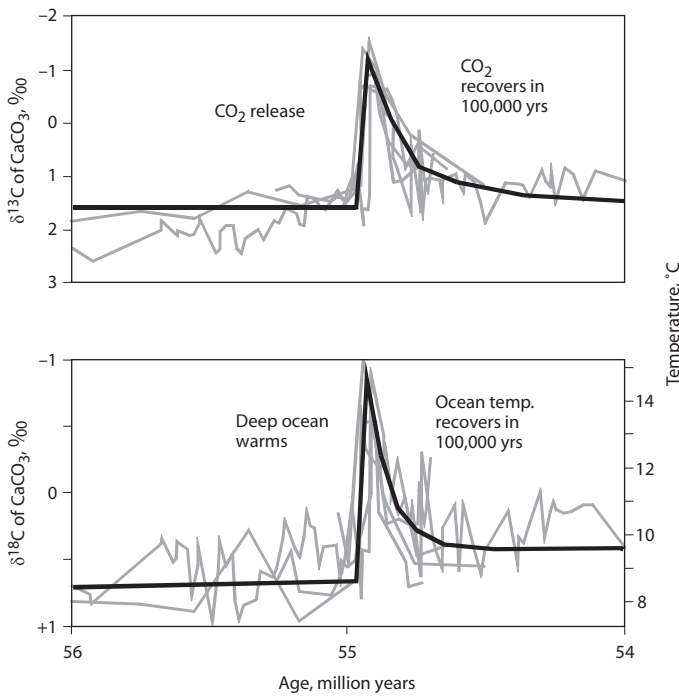


Figure 3. Data from the Paleocene-Eocene Thermal Maximum event. (Source: Zachos et al. 2001)

weathering of CaCO_3 (see box 2.3, “The World According to Carbon Isotopes”). The PETM climate event was initiated by a relatively sudden release of a large amount of isotopically light carbon, making the average $\delta^{13}\text{C}$ composition of the entire ocean about 2.5‰ lighter.

The isotopically light carbon is like a dye added to the ocean, which will flush through eventually as carbon is added to the Earth’s surface system by degassing from

Box 2.3**The World according to Carbon Isotopes**

The element carbon comes in three sizes. Two are stable, the abundant carbon-12 and the less abundant carbon-13. The third is carbon-14, which decays radioactively with a half-life of 5,730 years.

Carbon-14 is useful as a clock, remembering the last time the carbon in a sample saw the atmosphere. Carbon-14 is produced by cosmic rays as they impact nitrogen-14, the most common form of the most common element in the atmosphere. Plants grow from carbon from CO₂ in the atmosphere, with its carbon-14. Animals get their carbon from plants and are similarly carbon-14 hot. After a living thing dies, its carbon-14 is no longer replenished by growing or eating, and its stock of carbon-14 begins to decline. By measuring the abundance of carbon-14 relative to the rest of the carbon and knowing something about how the carbon-14 concentration in the atmosphere has varied through time, one can estimate the age of the sample. After a few half-lives, say 45,000 years, most of the carbon-14 decays away, no longer useful as a clock. Fossil fuels, for example, which typically are millions of years old, are called “radiocarbon dead.”

Carbon-14 dissolved in seawater reveals the circulation patterns of the ocean. Water with lots of carbon-14 in it sinks in the North Atlantic, and the oldest waters are found rising back to the ocean surface in the tropical Pacific Ocean. The carbon-14 of surface waters dates to an age of about 400 years, because the carbonate buffer system makes it very slow for the carbon isotopic composition of seawater to equilibrate with the atmosphere. The oldest waters in the ocean are about 1,500 years old.

The carbon-14 concentration in the atmosphere varies through time, in response to changes in the production rate

(Box 2.3 continued)

in the atmosphere, determined by the strength of the magnetic fields of the sun and the Earth, which shield the Earth somewhat from cosmic rays. Most of the carbon-14 produced on Earth finds its way into the ocean before it decays, and changes in the “ventilation rate” of the ocean also affect the concentration of carbon-14 in the atmosphere.

The stable isotopes of carbon, carbon-12 and carbon-13, are fractionated (separated somewhat) by biological processes. During photosynthesis, the enzyme that binds to CO_2 , called ribulose bis-phosphate carboxylase, or rubisco, chooses the lighter carbon-12 isotope about 2.5%, or 25‰ , more often than strictly chance. Organic carbon is therefore isotopically light, about -25‰ relative to a dissolved composition of near 0‰ on the PDB scale. When the carbon is converted to other biological molecules, its isotopic composition may change. Lipids (fats) are a bit lighter than proteins, for example, and when methane is produced biologically, the isotopic composition is near -60‰ . The spontaneously forming “thermogenic” methane is less fractionated, at about -30‰ . Inorganic carbon does not fractionate very much; the isotopic composition of CaCO_3 is very close to that of the carbon in the seawater from which it formed.

The isotopic compositions of organic carbon and CaCO_3 have been remarkably stable over geologic time. The isotopic separation between the two phases is set by the physical properties of a single enzyme, rubisco, the structure of which has apparently not changed much since the time of the very first sedimentary rocks from the early history of the Earth.

The absolute values of the CaCO_3 and organic carbon phases reflect the relative proportions of CaCO_3 and organic carbon weathering versus burial in the Earth. If carbon were weathered from an organic form in sedimentary

rocks, and then ultimately found its way into sediments as CaCO_3 , then it would pull the $\delta^{13}\text{C}$ of the ocean and the sedimenting CaCO_3 toward the light organic carbon value. The carbon isotopes tell us that the ratio of organic carbon to CaCO_3 buried globally on Earth is about 1:4, and that this ratio has been remarkably constant over geologic time.

Further reading: Broecker and Peng 1982.

the solid Earth and removed from the surface carbon cycle by weathering reactions. The recovery time for $\delta^{13}\text{C}$ was similar to the recovery time of atmospheric CO_2 from the weathering CO_2 thermostat theory: hundreds of thousands of years.

The oxygen isotopic composition of the CaCO_3 tells of a global warming event that seems quite analogous to the potential fossil fuel global warming event (see box 2.2, “The World According to Oxygen Isotopes”). Intermediate depths in the ocean, where the cores come from, show warming of perhaps 5°C . The average temperature of the surface of the Earth was also probably about 5°C warmer. The oxygen isotopic composition returned to normal in parallel with the carbon isotopic composition.

The correspondence between the recoveries of the carbon and oxygen isotopes indicates that, whatever the original source of the carbon, it was CO_2 that did the warming recorded in the sediment records. The other frequently accused greenhouse gas culprit is methane, but methane breaks down in about a decade in the sunlit, oxygenated atmosphere. The methane concentration could have been elevated during the short initial

release period, but it would have quickly subsided after the release was finished. The observation that $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ recovered in parallel fingers CO_2 as the culprit.

It's not clear where the slug of carbon came from or how much of it there was. It would be possible to estimate the amount of carbon if the isotopic composition of it were known, but different carbon reservoirs have different isotopic signatures. It would take more biological carbon, at an isotopic composition of about -20‰ , to generate the observed -2.5‰ change of the ocean than it would take of biologically produced methane, which has an isotopic signature of -60‰ .

One potential carbon source that has captured the imaginations of scientists and just about everybody else is methane hydrates in ocean sediments. There is a lot of carbon in these icy deposits, and it seems intrinsically unstable (see chapter 5). Methane has a relatively intense isotopic signature of about -60‰ , so it would take a smaller amount of carbon to generate the observed spike than if the carbon came from a less fractionated source. From biogenic methane, 2,000 Gton C would about do it.

The problem with hydrates as a carbon source is that 2,000 Gton C, added to the atmosphere and equilibrated with the ocean and with the ocean CaCO_3 pH-stat, would have increased atmospheric CO_2 from about 600 ppm during the warm Paleocene up to about 700 ppm for the long tail. The warming of 5°C inferred from the oxygen isotopes needs much more CO_2 change than that. A doubling of the atmospheric CO_2 concentration is

thought to warm the planet by about 2–4.5°C, but an increase from 600 to 700 ppm is much less than a doubling (see box 2.4, “The Climate Sensitivity Parameter”).

The severity of the warming would be easier to understand if the carbon came from a less isotopically fractionated source than methane. This would allow more carbon to be released to generate the observed carbon isotopic excursion. One possibility is that sedimentary organic matter could have oxidized to CO₂ when sea levels fell, leaving shallow-water sediments exposed to the atmosphere. Another is that peat deposits in soils could have burned or decomposed following some change in climate.

Climate scientists wonder if the Paleocene climate could have been more sensitive to changes in CO₂ than we believe today’s climate would be, perhaps because of some new positive feedback in the climate system (Pagani et al. 2006). This would allow a smaller CO₂ slug to be responsible for the warming indicated by the $\delta^{18}\text{O}$, while raising a frightening possibility that perhaps our present climate will turn out to be more sensitive than we think it is also.

The CO₂ released during the PETM acidified the ocean, as fossil fuel is doing today, and the result was a clay layer in the sediments, made up of materials left behind when the CaCO₃ dissolved (Zachos et al. 2005). Fossil fuel carbon is expected to leave a similar clay layer for paleoceanographers a million years from now, to mark the fossil fuel era. Consistent with the conclusion from the oxygen isotopes on the amount of warming,

Box 2.4**The Climate Sensitivity Parameter**

The climate sensitivity of the Earth is defined as the change in global average temperature of the surface of the Earth in response to a doubling of the CO_2 concentration of the atmosphere. It is written as ΔT_{2x} , and it was first estimated by Svante Arrhenius in 1896 to be about 6°C . The range from modern climate models participating in the latest International Panel on Climate Change model comparison exercise is $2.5\text{--}4^\circ\text{C}$ (Hegerl et al. 2007).

The idea of equilibrium here is tricky because there are some feedbacks in the climate system that respond almost immediately, such as the water vapor concentration of the air, and others that may take millennia, such as the growth and collapse of great ice sheets. The usual definition of the climate sensitivity parameter, as discussed in the context of global warming, allows several centuries for the temperature of the ocean to adjust to the changing CO_2 concentration, but not the full response of the ice sheets. The climate sensitivity of the Earth in the geologic past, including ice sheet changes, is probably higher than the human time scale global warming climate sensitivity.

Given an estimate of ΔT_{2x} , one can calculate the temperature response to a change in pCO_2 using the expression:

$$\Delta T = \Delta T_{2x} \times \ln(\text{new pCO}_2 / \text{orig. pCO}_2) / \ln(2).$$

Note that the temperature scales as the logarithm of the CO_2 concentration rather than linearly. This is due to the “band saturation effect,” which makes rare gases more powerful per molecule than abundant gases (see box 5.1, “Greenhouse Properties of CO_2 and Methane”).

the amount of CaCO_3 dissolved on the ocean floor seems to indicate that the carbon slug was bigger than 2,000 Gton C.

It is not clear how quickly the carbon was released, whether it came out all at once or over a time span as long as 10,000 years. The crucial issue for the biota in the ocean at that time is whether the CO_2 release took long enough for ocean invasion and neutralization by CaCO_3 to keep up. Those time scales are a few centuries for invasion and a few millennia for neutralization. If the CO_2 was released quickly compared with the ocean invasion time scale, there would have been a transient peak in atmospheric CO_2 , as there is today. If the CO_2 release was faster than the ocean pH-stat mechanism, there would have been a spike of acidity while the acidified ocean waited for the pH-stat to catch up, again as is expected for the fossil fuel CO_2 .

Since the amount of carbon released is not well constrained, it is difficult to draw conclusions from the PETM about the climate sensitivity of the Earth (see box 2.4, “The Climate Sensitivity Parameter”). Probably the firmest conclusion one can draw from the PETM is the longevity of the recovery of the $\delta^{13}\text{C}$ (CO_2 concentration) and the $\delta^{18}\text{O}$ (temperature). They recovered in parallel on a time scale on the order of 100,000 years, apparently confirming our understanding of the time constant for the weathering thermostat and the expected tail on the airborne fraction of CO_2 (see box 4.3, “Airborne Fraction of a CO_2 Slug over Geologic Time”).

Snowball Earth

Much earlier than the PETM, during a time when multicellular fossil-leaving critters were just fixing to enter the scene, Earth's climate took another jolt. About 600 million years ago, the Earth apparently froze over all the way into the low latitudes, into what climatologists call a "snowball Earth" (Hoffman and Schrag 2002). Ice and snow have a high albedo, meaning they are very reflective of visible sunlight, and the presence of ice tends to cool the planet. Once ice cover reaches about 30° North and South latitudes, Earth's climate should theoretically fall into a runaway cooling albedo feedback, quickly freezing all the way to the equator.

The frozen world allegedly stopped the hydrologic cycle. With no freshwater runoff to dissolve igneous rocks in, chemical weathering would have stopped removing CO₂ from the atmosphere. Degassing of CO₂ from the solid Earth continued, allowing the atmospheric CO₂ concentration to build up. It must have taken a lot of CO₂ to overcome the cooling albedo effect of the ice, and when the ice melted, the climate of Earth is thought to have flipped from a snowball to a hothouse very quickly. The elevated CO₂ concentrations would have driven prodigious rates of chemical weathering, resulting in global deposition of lots of CaCO₃ in what are called "cap carbonate" deposits, immediately on top of the glacial deposits.

Evidence for disruption of the biosphere comes from banded iron formations, deposits of iron that form when

oxygen invades an anoxic ocean. In anaerobic conditions, the stable chemical form for iron is as Fe^{2+} ion, which dissolves in water like sea salt. When Fe^{2+} reacts with oxygen, it becomes Fe^{3+} , which is insoluble in water and comes out as rust. Banded iron formations formed when oxygen first started building up in the atmosphere about 2 billion years ago, but not since then, except for the end of the snowball, 0.6 billion years ago. The idea is that complete ice cover isolated the ocean from the atmosphere, allowing it to go more completely anoxic than it could without the ice cover.

The weathering CO_2 thermostat can explain a recovery from a snowball Earth climate event. What is still unexplained is how the event started in the first place. Normally, Earth's temperature is controlled by the weathering CO_2 thermostat; cooling leads to a decrease in weathering, allowing CO_2 to build up in the atmosphere. Maybe something pushed the climate to be cold faster than the weathering thermostat could keep up. One enticing suspect is atmospheric methane (see chapter 5).

Life Span of the Biosphere

Another interesting twist comes from connecting the dots between the weathering CO_2 thermostat and the brightening of the sun through time. Imagine the heat source of a pizza oven growing slowly hotter and the insulation around the oven slowly melting away in response, not just randomly but in a regulated way, resulting in a constant oven temperature for baking the pizza

inside. This is how the weathering CO_2 thermostat has been functioning. The end of the biosphere comes when the CO_2 concentration has to go too low to support life—in particular, to support photosynthesis (Lovelock and Whitfield 1982).

Plants have evolved a new system for pumping CO_2 into the photosynthetic machinery, called the C-4 pathway, as opposed to the original system, called C-3. Grasses are C-4 plants, and they can tolerate much lower CO_2 levels than C-3 plants can, about 10 ppm for C-4 versus 200 ppm for C-3. C-4 plants supercharge the CO_2 concentration inside the cell, allowing the plant to grow in lower CO_2 conditions. The names C-3 and C-4 come from the three- and four-carbon sugar molecules that the CO_2 first becomes incorporated into in each pathway.

The C-4 pathway apparently evolved as many as forty different times, independently in different plant lineages, an amazing example of convergent biochemical evolution. C-4 is a relatively recent development, about 30 million years old, while land plants in general have been around for more than 400 million years. Interestingly, atmospheric pCO_2 during the glacial time reached as low as 180 ppm, within spitting distance of being too low for the C-3 plants. It might be expected that C-4 plants would start to take over during the low- CO_2 glacial times, but there's no evidence for such a change.

The forecast (for the demise of the biosphere by dropping CO_2 levels driven by heating up of the sun) is for very slow progress along that direction, with the final

gasp scheduled for about 1 billion years from now (Caldeira and Kasting 1992).

ORGANIC CARBON AND OXYGEN

The carbon cycle apparently controls the oxygen concentration of the atmosphere on geologic time scales of millions of years and longer. Early Earth had no oxygen in the atmosphere, and it still would not if it were not for life on Earth. The source of oxygen for the atmosphere, and any mechanism for explaining how it is regulated, has to do with chemical changes of carbon and other elements, involving electrons, in reactions called oxidation and reduction reactions (see box 1.3, “Oxidation and Reduction of Carbon”).

Photosynthesis takes oxidized carbon (CO_2) and chemically reduces it to make organic matter, something like CH_2O (see box 1.4, “Photosynthesis and Respiration”). Since electrons cannot simply appear out of nowhere, the reduction of carbon (gaining of electrons) must be accompanied by the oxidation of some other element (where the electrons come from). Multicellular creatures such as ourselves are limited to oxygen/water as the complementary oxidatized/reduced couple. Bacteria, however, can use many other chemistries to go with the oxidation and reduction of carbon, such as sulfate (SO_4^{2-})/sulfide (H_2S) and nitrate (NO_3^-)/nitrogen gas (N_2). Iron cycling between Fe^{3+} and Fe^{2+} seems to have been important in the earliest photochemical reactions by bacteria in the early Earth. But iron was in limited

supply, and probably limited the rate of iron-based biochemistry (De Duve 1995).

What an innovation it was when the biochemical playbook of life on Earth developed the ability to split water to get electrons (Holland 1984). Water is always abundantly available, or if it wasn't a bacterium had to worry about drying out anyway. But the by-product was molecular oxygen, O_2 . This is explosive stuff, handled extremely carefully by organisms that base their metabolism on it, which includes all multicellular organisms. Some forms of bacteria are unable to tolerate molecular oxygen at all. Forms of life that reigned supreme on Earth for billions of years were chased off into the darkest corners of the biosphere by the oxygen pollution, into the darkest muds and swamps. It was as if some branch of the tree of life today reaped a huge competitive advantage by producing chlorine gas out of chloride in sea salt, chasing all of us into hiding forever.

Oxygenic photosynthesis performs the following chemical reaction:



where the energy comes from sunlight (see box 1.4, "Photosynthesis and Respiration"). The back-reaction is called respiration when organisms such as ourselves do it, by eating food and breathing oxygen. A similar chemical reaction is behind the harvesting of fossil energy industrially; then it is usually done by combustion.

Most of the carbon "fixed" by photosynthesis is destined to be respired quickly, decomposing in the soils

most likely or perhaps winding up in a molecule of beer, and being converted back to CO_2 in the liver of a beer drinker (Volk 2008). When organic carbon is respired, it consumes the same amount of oxygen as was produced when the organic carbon was first grown in the plant.

The only way to generate oxygen that can build up in the environment is to protect the carbon from getting re-oxidized. Most parts of the land surface do not bury very much organic carbon for the long haul. Peat deposits can preserve organic carbon for tens of thousands of years, but the main place to dispose of organic carbon for the long geologic haul is in the sediments of the ocean.

The first signs of molecular oxygen date back to about 2 billion years ago, a bit less than half the age of Earth now (Canfield, Habicht, and Thamdrup 2000). But before free oxygen could accumulate in the atmosphere, a lot of chemical changes had to happen, in particular in the oceans. Iron was dissolved in seawater in the form of Fe^{2+} , along with the rest of the sea salts. When Fe^{2+} sees oxygen, it gives up an electron to become Fe^{3+} , which forms insoluble rust-like compounds, the banded iron formations mentioned in reference to snowball earth. Sulfur was previously insoluble in the ocean, in the chemical form of sulfide, H_2S , which crystallizes with the dissolved iron in the ocean to make pyrite, FeS_2 . As the oxygen invasion continued, sulfur began to accumulate in the ocean as oxidized sulfate, SO_4^{2-} . In the end, 80% of the oxygen ever produced went toward paying the “oxygen debt” of the planet, oxidizing the iron and the sulfur, before oxygen could begin to accumulate in the atmosphere.

At the rate at which organic carbon is being buried in ocean sediments today, the biosphere could double the oxygen content of the air in about 2 million years. Fortunately for us, the oxygen left behind when a remnant of plankton becomes buried in the mud is balanced by the uptake of oxygen by reaction with some other ancient fossil piece of plankton that was buried millions of years ago. In the language of geochemistry, on a long-term average, the global burial of organic carbon must be balanced by oxidative weathering of sedimentary organic carbon. If it were not balanced, the oxygen concentration in the air could get seriously out of whack within a few million years, whereas we know it's been pretty stable for hundreds of times longer than that.

The isotopic compositions of organic carbon and CaCO_3 through time tell of the proportions of carbon in these two forms, and with a few short exceptions they are buried in a very constant global ratio of about 4:1 (see box 2.3, "The World According to Carbon Isotopes"). When there are excursions in carbon isotopes, there are usually also complementary excursions in the isotopes of sedimentary sulfur. There is an oxidized form of sulfur in the sediments, which is gypsum (CaSO_4), and a reduced form, pyrite (FeS_2). These forms are analogous to the oxidized and reduced forms of carbon in the sediments, CaCO_3 and organic carbon. If sulfur is weathered in the form of gypsum and buried in the form of pyrite, it will leave behind O_2 , just as the burial of reduced carbon does.

According to carbon and sulfur isotopes, at times when organic carbon burial happens to be high, the rate

of reduced sulfur burial tends to be low, offsetting the net source of O_2 to the atmosphere that would arise from the organic carbon burial alone (Berner 2006). The anticorrelation between organic carbon and reduced sulfur burial is further evidence for an atmospheric or oceanic oxygen-regulating mechanism. If oxygen in the atmosphere is like a battery, then the battery is on a charger (driven by burial of organic carbon today), and apparently it is a regulated one.

The regulator of the oxygen battery charger probably mostly has to do with the effect of oxygen on the burial of organic carbon (Cappellen and Ingall 1996). Animals and bacteria use the oxygen and the organic carbon as an energy source, just as we are doing when we eat lunch. If you take away the oxygen, it takes us multicellular critters out of the picture. Bacteria can still eat the organic carbon, reacting it with other chemistries based on sulfur, iron, nitrogen, or hydrogen gas, but the bacteria are apparently less efficient at scrubbing away all of the organic carbon from the mud, allowing more of it to be buried. A scarcity of oxygen in the air would make the ocean anoxic, leaving more organic carbon uneaten in sediments, resulting in more oxygen left behind to bring the atmospheric concentration back up.

The oxygen concentration of the atmosphere may drift up and down a bit through geologic time, perhaps reaching a concentration twice its present-day value. There isn't much proxy constraint on oxygen changes of this magnitude. One suggestion comes from dragonflies and other insects, which reached enormous size in the

Cretaceous. These bugs rely on diffusion to carry oxygen to their body interiors rather than on a circulation system, so their size is strictly limited by the concentration of oxygen in the air (Graham 1995). However, if oxygen got too much higher than twice its present concentration, it would start leading to continental-scale forest fires, leaving traces such as charcoal that would probably have turned up in the geologic record.

The oxygen homeostat is not as well understood as the weathering CO_2 thermostat, in that there are ideas but no detailed models for oxygen yet. There are detailed models for the CO_2 thermostat, but they are not as well pinned down by data and well-developed theory as are, for example, the climate models on which the forecast for global warming is based.

Vagaries of the oxygen homeostat have probably clobbered the biosphere a few times in the past, but the evidence is thin and the constraints rather shaky. There are times when large regions of the ocean went anoxic for a few million years at a time, leaving behind layered sediment deposits, undisturbed by burrowing organisms because they don't live in anoxic conditions, and generally higher concentrations of organic carbon in the sediments. The deep ocean went anoxic as part of the PETM climate event 55 million years ago (Kennett and Stott 1991), for example, and during the event that killed the dinosaurs at the Cretaceous/Tertiary (K/T) boundary 65 million years ago (Handoh and Lenton 2003). The largest extinction event of all occurred 255 million years ago, at the end of the Permian era. This was so long ago that it is

particularly shrouded in mystery, but some of the usual suspects have to do with chemical components such as hydrogen sulfide (H_2S) or CO_2 that could have built up in a stagnant anoxic ocean (Knoll et al. 1996).

There must be some coupling between the weathering CO_2 thermostat and the oxygen homeostat because both involve carbon. Global warming from fossil fuel combustion is an example of the organic carbon system perturbing the CO_2 thermostat. The PETM is apparently another example. In both of these events, the organic carbon cycle perturbs the CO_2 concentration for as long as the weathering CO_2 thermostat will allow it, a few hundred thousand years.

Changes in organic carbon burial might affect the set-point of the weathering CO_2 thermostat. The CO_2 thermostat balances carbon fluxes into and out of the Earth, and organic carbon is an alternate carbon flux back into the Earth, in addition to the CaCO_3 product of weathering. Organic carbon burial is driven by accidents of continental geometry such as the abundance of shallow-water seas and river deltas. If suddenly the Earth began burying more organic carbon, the imbalance of carbon fluxes would pull the CO_2 concentration down until the rate of weathering slowed enough to rebalance the fluxes.

The biosphere can only increase or decrease the rate of organic carbon burial for about a million years or so, however, because an imbalance in organic carbon burial would produce or consume atmospheric oxygen. Since atmospheric oxygen hasn't changed very much, the organic carbon burial rate must be regulated. If it gets out

of whack it'll get pulled back into line. In short, changes in the amount of organic carbon buried on Earth, such as by the combustion of fossil fuels, can have a huge impact on the climate of Earth, but for a limited time only.

COMING HOME TO THE QUESTION OF GLOBAL WARMING

Fossil fuel carbon will ultimately return to the solid Earth by means of the weathering CO_2 thermostat (see box 4.3, “Airborne Fraction of a CO_2 Slug over Geologic Time”). The 100,000-year time constant for the CO_2 thermostat means that global warming will persist for something like this long, similarly to the PETM event. The longevity of global warming will have particular impact on the slowest-changing components of the climate system, of which the major ice sheets are the prime example. The future of the global warming climate event is the topic of chapter 4.

3 THE UNSTABLE ICE AGE CARBON CYCLE

The carbon cycle on time scales of the glacial/interglacial cycles seems to have a different character than it does on million-year time scales. Here it tends to amplify climate changes driven by orbital forcing. A cold climate as determined by a cool orbital configuration tends to drive the atmospheric CO_2 down, making the climate even colder. The mechanisms by which the carbon cycle accomplishes this are not clear. Some current thinking on the question is reviewed in this chapter.

BACKSTORY

Ice and sediment cores provide records of 100,000-year cycles of ice sheet growth and collapse known as the glacial/interglacial cycles. Ice sheets also contain bubbles, ancient air samples that can be analyzed for past atmospheric CO_2 concentrations. The longest record yet constructed is from Vostok research station in Antarctica. It goes back through eight glacial/interglacial cycles (Siegenthaler et al. 2005) (figure 4). Atmospheric CO_2 is

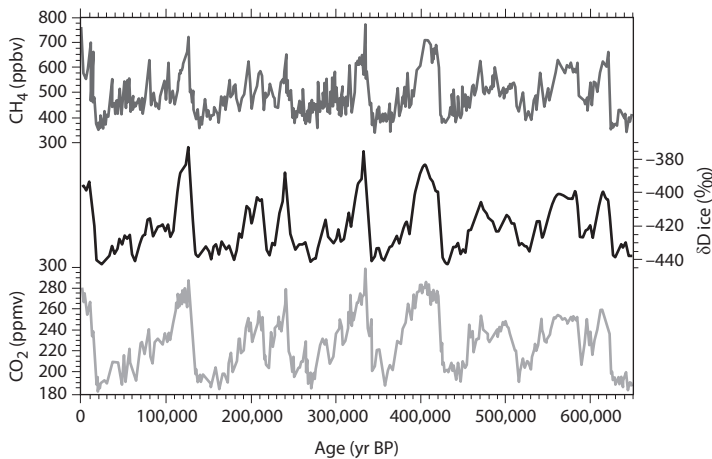


Figure 4. Ice core CO_2 , methane, and temperature records, from EPICA. (Source: Siegenthaler et al., 2005)

strongly correlated with global climate, as if the carbon cycle were amplifying the climate changes that are driven originally by wobbles in the Earth's orbit around the sun.

It is something of an anomaly in Earth's history for large ice sheets to exist at all. Throughout most of Earth's history, the climate of the surface of the Earth was warmer than it is today. Driven by slow changes in the geometry of the plates of the Earth's crust, the climate of the Earth drifts between hothouse climates, warm to the poles, to icehouse climates with cold poles and ice sheets, as today. Our current icehouse began with the formation of the ice sheet on Antarctica 35 million years ago as part of a long-term cooling trend that began about 50 million years ago (Zachos et al. 2001).

More recently, about 3 million years ago, ice sheets started forming in the Northern Hemisphere, such as the ice sheet that now covers nearly the entirety of Greenland. North America sported the Laurentide ice sheet and northern Europe the Fennoscandian ice sheet, which grew to rival the great ice sheets that exist today in Antarctica and Greenland and then collapsed, melting away entirely during the warmer but shorter interglacial interval. The Greenland and Antarctic ice sheets also grow and melt back partially in synchrony with the glacial cycles.

The continental crust floats atop the roiling convection of the Earth's mantle like slag, the buoyant impurities on the surface of molten metal at a steel refinery. The total area of continental crust seems to be fairly stable though time, at least for the last half billion years, when the presence of fossils makes it possible to reconstruct the surface of the Earth in greatest detail, but the distribution of the land surface changes in climatically significant ways.

Today there is more land area in the Northern Hemisphere than in the Southern Hemisphere, and this configuration drives much of the character of the glacial climate cycles. At other times in Earth's history the land was mostly found along the equator, or bunched together into a single supercontinent such as Pangaea, 250 million years ago. Ocean passageways open and close, such as the current open-water pathway around the world in the Southern Ocean or a past connection, now blocked, between the Atlantic and Pacific oceans

through Panama. These geometry shifts had similar or even stronger impacts on climate than our current north-heavy distribution does.

The world was a different place during the Last Glacial Maximum, about 18,000 years ago. The ice sheets held so much water that sea level was about 120 meters lower than today. The average depth of the continental shelves, low-lying seafloor plains at the edges of some parts of the continental crust, is about 100 meters. Large areas of continental shelf were exposed during the Last Glacial Maximum, forming bridges between Russia and Alaska and between Britain and France (Fagan 2004).

The glacial climate changes were more dramatic in the Northern Hemisphere than in the Southern Hemisphere because there is more land in the Northern Hemisphere where ice sheets could potentially form. But the climate of the entire Earth warms and cools more or less together through the glacial cycle. The land of Europe not covered in kilometers of ice was a windswept, occasionally inhabitable plain. Anatomically modern humans occasionally entered the region, following a nomadic hunting lifestyle, but they retreated when the climate turned harsher.

According to the climate archives of the ice and sediment cores, the glacial climate state was tippier than the warmer, interglacial state (Alley 2000). The climate of Greenland in particular, representative of conditions in the North Atlantic, flip-flopped rhythmically in a 1,000-year sawtooth pattern, with abrupt warmings called Dansgaard-Oeschger events. These events in turn were

punctuated by periodic collapses of the Laurentide ice sheet into the Atlantic, called Heinrich events. The details are still murky of how these so-called abrupt climate changes worked, but they probably involved ingredients of the overturning circulation of the North Atlantic, driven by deep-water formation, and changes in the sea ice cover in the Atlantic. These abrupt climate changes pose a warning to us about future climate changes, which are projected by the models to be a smooth response to rising greenhouse gas concentrations, even though the climate forcing today is changing the climate more rapidly than it ever did naturally. If the natural climate can flip-flop so abruptly, then maybe it can do so again in our future.

The timings of the comings and goings of the ice sheets correlate with variations in Earth's orbit around the sun, the so-called Milankovich cycles (Imbrie and Imbrie 1979). The wobbles in Earth's orbit don't change the total amount of sunlight that the Earth receives by very much, but they change the distribution of the sunlight as a function of latitude and day of the year. The sweet spot for glacial climate cycles seems to have been the northern latitudes, about 65°N, at about the summer solstice. Changes in sunlight intensity at this time seem to be calling the shots, beating the drum that the glacial cycles are marching to.

The relationship between solar forcing and the growth or dissolution of ice sheets, however, is not simple (Pailard 2001). The amount of ice is not a straightforward function of sunlight intensity, nor is the rate of ice

growth or melting. Rather, an ice sheet seems to have a life cycle, which is paced by variations in the intensity of the sunlight. When an ice sheet first forms, or “nucleates,” it changes the albedo of the land surface, cooling the surroundings and stabilizing its own existence. The nucleation of ice sheets seems to require a trigger of especially weak sunlight in the Northern Hemisphere summer. Once it nucleates, an ice sheet seems to persist regardless of changes in conditions until it reaches a size large enough that it begins to melt at the base, becoming vulnerable to a warm-trigger sunshine intensity, at which point it collapses.

THE GLACIAL CARBON CYCLE

The CO_2 concentration of the atmosphere has been revealed in the ice cores to go up and down in synchrony with the glacial state of the Earth. During the Last Glacial Maximum, atmospheric CO_2 was between 180 and 200 ppm for a time period 50,000 years long. The pre-industrial concentration in the year 1750 was about 280 ppm, and the ice core record shows that the CO_2 concentration of the last interglacial time, 120,000 years ago, was also about 280 ppm. The CO_2 concentration has been rising and falling, along with the temperature of the Earth and the level of the oceans.

The lower CO_2 concentration is about half the reason why the Earth was colder during the Last Glacial Maximum (Jansen et al. 2007). The other half of the glacial climate forcing comes from albedo changes from sea ice

and ice sheets. Atmospheric CO_2 changes also presumably globalize the glacial cycles. A property of the orbitally driven variations in sunlight intensity is that they are antisymmetric about the equator. Cool summer sunlight in the Northern Hemisphere will be complemented by warm summer sunlight in the Southern Hemisphere. Yet the temperature of the entire Earth rises and falls along with the Northern Hemisphere forcing. To some extent, this is because the Northern Hemisphere is where the land is to form ice sheets, but the CO_2 concentration of the atmosphere also ties the climate of the Earth together globally.

The natural CO_2 concentration generally takes a thousand years or longer to change. One thousand years is about how long it takes for the atmosphere and the ocean to reach equilibrium with each other (see box 4.2, “Air-Sea Exchange of CO_2 Gas”). Today, we are putting CO_2 in the atmosphere on a time scale that is faster than this, and the ocean is taking it back out of the atmosphere, striving for a new equilibrium. In contrast, the thousand-year and longer time scale of the natural CO_2 changes documented in the ice cores seems to suggest that they were driven by changes in the equilibrium partitioning of CO_2 between the air and the sea.

The history of the ice sheets and atmospheric CO_2 has cycles in it as long as 100,000 years. This is just shorter than the equilibration time scale of the weathering CO_2 thermostat described in chapter 2. Some trick of the carbon cycle drew down atmospheric CO_2 for a while, but it couldn't have done it for too much longer because

it would have been swimming against the tide of the weathering CO_2 thermostat mechanism. Both fossil fuel CO_2 added to the atmosphere and the glacial cycles in atmospheric CO_2 are analogous to a sunbeam alternately warming and cooling a house faster than the house's thermostat can keep up.

It appears as if the carbon cycle, manifested in the CO_2 concentration of the atmosphere, and the temperature of the Earth, are coupled in a two-way loop of potential cause and effect. The direct physical link between solar intensity and the size of the ice sheets makes it seem as though the carbon cycle is acting in a following role, amplifying the climate changes from the ice sheets by building up in the atmosphere when the climate warms and withdrawing from the atmosphere when it cools. Instead of stabilizing climate, as it does on million-year time scales, the carbon cycle seems to be exacerbating the glacial climate swings.

The clearest transition in atmospheric CO_2 in the ice core record is the rise in CO_2 concentration from the low 200 ppm concentration from the Last Glacial Maximum to a higher, Holocene concentration of about 260 ppm 10,000 years later (followed by a slow rise to our pre-anthropogenic 280 ppm until about the year 1750, then the abrupt anthropogenic rise to about 390 today). The relative timing of the CO_2 and temperature rises is obscured a bit by the fact that CO_2 is measured in the bubbles, while the proxy for local temperature is the oxygen isotopic composition in the ice. Because bubbles don't seal from the atmosphere until they are some 50 meters

below the surface of the snow, the bubbles end up holding air that is a few centuries younger than the age of the ice the bubbles are trapped in.

One approach to dealing with this problem was to develop a proxy for temperature changes in the ice based on measurements made in the bubbles: specifically, subtle variations in the abundances of nitrogen isotopes in the bubbles (Severinghaus 1998). If the surface of the ice sheet warms suddenly, there will be a period of a few decades when ice is colder down by where the bubbles are closing off than it is up at the surface. During that time, the process of gas diffusion through the snow generates a difference between the gas composition in the bubbles relative to the atmosphere. A spike in nitrogen isotopes in the bubbles means there was a sudden warming at the surface.

The gas compositions in the ice core bubbles show that the temperature in Antarctica started rising about 800 years before the CO_2 concentration started to rise. In the end, the transitions of both took 10,000 years, so there is room in the data for the rise in CO_2 to play a role in most of the warming of the deglacial transition, as well as for the temperature of the Earth, in particular perhaps the temperature of the Southern Ocean, to drive changes in atmospheric CO_2 . One often reads on the Internet the temperature lead cited to suggest that CO_2 has no effect on climate, but that is a silly argument, because there is no reason why the direction of cause and effect can only go one way or the other. A feedback loop is by definition a loop of cause and effect, and it happens all the time.

Carbon isotopes (see box 2.3, “The World According to Carbon Isotopes”) can tell us something pretty fundamental, that the change in atmospheric CO_2 was not driven by uptake and release of carbon from biomass or any other form of organic carbon. The $\delta^{13}\text{C}$ of organic carbon is typically about $-25^\circ/\text{‰}$, while the dissolved CO_2 from which photosynthesis draws carbon is near $0^\circ/\text{‰}$. If the atmospheric CO_2 drawdown during glacial times were due to production of organic matter, we would expect the carbon left behind in the ocean to be isotopically heavier, reflecting the carbon-13 left behind. Instead, the $\delta^{13}\text{C}$ of the CaCO_3 produced in the deep ocean was lighter during glacial times; the value changed by about $-0.25^\circ/\text{‰}$. The carbon isotopes say that there was a release of carbon from an organic source during glacial times, not an uptake. The biosphere exhales when we would prefer it to inhale (Shackleton et al. 1983).

Crunching the numbers, to lighten the ocean, changing $\delta^{13}\text{C}$ by $-0.25^\circ/\text{‰}$ would require about 500 Gton C of carbon that had an isotopic composition of $-25^\circ/\text{‰}$ (see box 1.2, “Reservoirs of Carbon,” and box 2.3, “The World According to Carbon Isotopes”). The favored source among climate scientists is the terrestrial biosphere, the trees and soil carbon on land, which together with the soils hold about 2,000 Gton C today. Models of the terrestrial biosphere predict at least this much change in biomass in response to the change in climate and retreat of the ice sheets. There is also a significant amount of dissolved organic carbon in the ocean, and lots of methane

in ocean sediments, which are isotopically light and would also affect the whole-ocean $\delta^{13}\text{C}$ if they had released carbon during glacial time.

How much impact would 500 Gton C have had on the atmosphere? To estimate that kind of thing it is important to pay attention to the time scale. The glacial cycles took tens of thousands of years, which is longer than the atmosphere ocean equilibration time scale (centuries), and longer than the CaCO_3 pH-stat time scale (a few millennia). From box 4.3, "Airborne Fraction of a CO_2 Slug over Geologic Time," the airborne fraction of a slug of CO_2 added to the carbon cycle, after CaCO_3 equilibration, is about 10%. Adding 500 Gton C and waiting a few millennia would result in about a 50 Gton C increase in the atmospheric inventory. A handy conversion factor for doing these carbon cycle- CO_2 calculations is that 1 Gton C added to the air changes the CO_2 concentration in Earth's atmosphere by about 0.5 ppm. So the release of carbon by the land surface during glacial times would have increased the CO_2 concentration of the air by about 25 ppm.

We were originally trying to explain why the CO_2 concentration in the air during glacial times was 80 ppm lower, and we came up with a factor that would instead make the CO_2 higher by 25 ppm—the wrong direction to explain the ice core CO_2 data. The conclusion is that the glacial cycles in atmospheric CO_2 must originate from the inorganic carbon cycle, meaning the ocean, and it must be strong enough to overcome the push in the opposite direction from the organic carbon cycle.

THE OCEAN DID IT, BUT HOW?

Changes in Ocean Temperature

The simplest mechanism for driving the atmospheric CO_2 cycle, one that at least goes in the right direction, is based on the higher solubility of gases in colder water than warmer (see box 3.1, “Carbonate System pH Chemistry”). If you just take a bucket of seawater and warm it up 1°C , its pCO_2 value, which is the equilibrium partial pressure of CO_2 that the air above it would reach, increases by about 4%. CO_2 molecules that are excited by thermal energy would prefer to be untethered in the gas phase rather than bogged down in the liquid.

The equilibrium state between the atmosphere and the ocean is complicated by the fact that ocean water comes in a wide range of temperatures. The water flows around, warming up in some places and cooling down in others. When seawater warms up, it tends to push CO_2 out, into the atmosphere, balanced in equilibrium by CO_2 dissolving in the ocean in some location where the water is cooling down. The heat fluxes and temperature variations in the surface ocean are the drivers of enormous back-and-forth exchange flux of CO_2 between the atmosphere and the ocean.

The distribution of CO_2 between the atmosphere and the ocean might respond to changes in the way that the waters flow in the ocean. Leaving that aside for the moment, and taking the circulation and mixing of the ocean waters as a constant, models of the carbon cycle in the

Box 3.1**Carbonate System pH Chemistry**

When CO_2 dissolves in H_2O it enters the domain of a coupled series of pH reactions that stabilize the CO_2 concentration and determine the pH of the water. These chemical reactions can be described using tools of equilibrium thermodynamics, which entails calculating what the lowest energy configuration would be for a given set of ingredients.

The first-order picture, called the ideal calculation, takes the chemical availability or activity of some chemical species such as dissolved CO_2 as proportional to the concentration. For dissolved CO_2 , the ideal activity is counted as the number of moles of CO_2 per liter of the solution. For CO_2 gas, the ideal activity would be calculated as the pressure exerted by just the CO_2 molecules in the air, called the partial pressure of CO_2 , which is equal to the total pressure of the air times the fraction of the air molecules that are CO_2 .

Ideally, after air and water have had time to equilibrate, the amount of CO_2 in the gas phase will go up and down in direct proportion to any changes in the concentration of the dissolved CO_2 in the solution, the water phase. This is known as Henry's law:

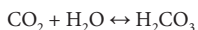
$$p\text{CO}_2/\text{CO}_2 (\text{aqueous}) = K_H.$$

However, if concentrations or pressures become large enough, or if the molecules interact chemically with other molecules, then reality can begin to deviate from the ideal calculation, at which point we require fudge factors called activity coefficients. These are corrections to the concentration or the pressure to account for their apparent availability. For a specific set of conditions, for example chemical conditions close to seawater, these activity coefficients can be folded into "apparent"

(Box 3.1 continued)

equilibrium constants, denoted by a prime, such as K'_H . The values of the apparent equilibrium constants for seawater depend on the salinity as well as temperature.

CO_2 combines with water in a hydration reaction to form carbonic acid, H_2CO_3 :



In practice, for calculations, the concentrations of dissolved CO_2 gas and hydrated dissolved CO_2 (the carbonic acid, H_2CO_3) are usually lumped together and called H_2CO_3^* . On reflection, I'm not sure why this is done. The hydration reaction is slower than the pH reactions, and its biological importance is demonstrated by an enzyme to speed the reaction up, called carbonic acid anhydrase. At any rate, in practice, H_2CO_3^* stands in for the concentration of CO_2 in the aqueous phase in Henry's law. Acknowledging also nonideal chemical effects by using an apparent Henry's law coefficient, we now have:

$$p\text{CO}_2/\text{H}_2\text{CO}_3^* = K'_H,$$

where the $p\text{CO}_2$ is the ideal pressure of CO_2 , ($p\text{CO}_2$), in the gas phase, proportional to the numerical ratio of CO_2 molecules in the gas (as in ppm).

It is common to talk about a $p\text{CO}_2$ of a parcel of seawater, based on this equation, which is the equilibrium CO_2 pressure in a hypothetical gas phase if it existed. If the $p\text{CO}_2$ of the surface ocean is higher than the $p\text{CO}_2$ of the air, CO_2 will evaporate from the water into the air. The air-sea flux is proportional to the difference in $p\text{CO}_2$ between the air and the water (see box 4.2, "Air-Sea Exchange of CO_2 Gas").

Acids release free protons, H^+ , into the water, lowering the pH of the solution, defined as the $-\log_{10}$ of the H^+ activity (ideally, concentration). Carbonic acid can release a pair of

protons to form bicarbonate ion, HCO_3^- , and carbonate ion, $\text{CO}_3^{=}$. The reactions are:



These pH reactions are fast enough that equilibrium thermodynamics pretty much always apply. Thermodynamics gives us one equation for each of the two reactions:

$$[\text{H}_2\text{CO}_3]/([\text{H}^+][\text{HCO}_3^-]) = K'_1 \quad (3)$$

$$[\text{HCO}_3^-]/([\text{H}^+][\text{CO}_3^{=}) = K'_2 \quad (4)$$

where K'_1 and K'_2 are the first and second dissociation constants for carbonic acid, corresponding to reactions 1 and 2, with the primes denoting that they are apparent values corrected for nonideality.

These reactions together form a chemical buffer system that controls the pH (acidity) of seawater and allows seawater to hold more CO_2 than it would otherwise. There is a lot more dissolved carbon in seawater than H^+ , so that changes in H^+ concentration, in moles per liter, will be much smaller than the moles per liter changes in the dissolved carbon. The best way to understand how CO_2 dissolves in buffered seawater is to combine the dissociation reactions to eliminate sources or sinks of H^+ , because it is such a small reservoir, leaving



This reaction takes about a minute to find equilibrium, limited by the hydration reaction; the deprotonation reactions are much faster. If you add or remove one of the reaction participants, the new equilibrium will shift in the direction of compensating for the addition or removal. Adding CO_2 to seawater, for example, tends to shift this reaction to the right, consuming CO_2 and $\text{CO}_3^{=}$ and producing HCO_3^- .

(Box 3.1 continued)

The amount of CO_2 that seawater can absorb is controlled by the amount of $\text{CO}_3^{=}$ that is available for CO_2 to react with. Ions such as bicarbonate and carbonate are salts that do not evaporate into the atmosphere as CO_2 can, since ions are only found in solution. $\text{CO}_3^{=}$ is acting like a chemical base, scrubbing CO_2 from the air, the way CO_2 is scrubbed from the air in submarines and space ships.

There is about 10 times more $\text{CO}_3^{=}$ than there is dissolved CO_2 (H_2CO_3^*). This means that if you double the pCO_2 in the air and equilibrate it with a bucket of seawater, the seawater will take up about ten times more CO_2 than it would have if there were no buffer chemistry, and Henry's law were the only thing going on. About 90% of the CO_2 that dissolves in the seawater reacts with $\text{CO}_3^{=}$ to form HCO_3^- .

As the pCO_2 in the air rises, the concentration of H_2CO_3 rises according to Henry's law, and the concentration of $\text{CO}_3^{=}$ drops proportionally. As the $\text{CO}_3^{=}$ in the ocean is depleted, the ocean loses its CO_2 buffering strength, leading to an inevitable decline in fossil fuel CO_2 uptake by the oceans.

The carbonate equilibrium reactions control the pH of the solution, as they also do in our blood and cell plasma fluids. The H^+ concentration of the seawater depends on the ratios of the various carbonate species, as in, for example:

$$[\text{H}^+] = [\text{H}_2\text{CO}_3]/(K'_1 [\text{HCO}_3^-])$$

from the equilibrium condition (3) for the first dissociation reaction (1). As CO_2 invades seawater, the H^+ concentration rises and the pH drops. This is called ocean acidification.

The $\text{CO}_3^{=}$ concentration decreases with acidification, affecting marine life through the reaction



This is the equilibrium reaction that determines whether shells made of CaCO_3 should dissolve or not. Corals make CaCO_3 , as do phytoplankton in the open ocean. As the ocean becomes acidified, it gets harder to make and maintain shells of CaCO_3 .

The rising concentration of dissolved CO_2 may also affect metabolic chemistry directly. CO_2 is the building block for respiration, and higher concentrations could boost photosynthesis the way they can on land. CO_2 is also the waste product of respiration that has to be exhaled, which is in principle harder at higher ambient concentrations.

A rising H^+ concentration itself may also affect biological systems. The pH of the surface ocean has decreased by about 0.1 pH units owing to human release of CO_2 . The logarithmic scale of pH tends to understate the change, which in concentration of H^+ has already increased by 25% in surface ocean waters. H^+ is an aggressive chemical reactant and a key player in many other chemical couples in the natural world, affecting metals, minerals, and biomolecules.

Total CO_2 and Alkalinity of Seawater

The inorganic carbon chemistry of seawater is nonlinear in that water with an H_2CO_3^* concentration of, say, 10 micromolar, added in equal proportion to another sample of 20 micromolar, does not necessarily yield a solution of 15 micromolar. Each solution buffers the H_2CO_3^* concentration and the pH at some value, and when they are mixed, the result is a combination of the two buffer chemistries, which is not a linear or simple function of the sum of the parts.

Two derived quantities make it much easier to think about the effects of processes such as plankton growth on the CO_2 chemistry of seawater. The first is the total CO_2 concentration, defined as the sum of all the inorganic species:

(Box 3.1 continued)

$$\Sigma\text{CO}_2 = [\text{CO}_2] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{=}],$$

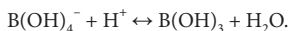
where the square brackets denote concentrations (moles/liter). The ΣCO_2 concentration doesn't care about anything that pH changes can do because ΣCO_2 takes the sum of all the possibilities. When CO_2 dissolves in seawater, it adds to the ΣCO_2 . When carbon is removed, to make organic carbon or CaCO_3 or whatever, the ΣCO_2 concentration declines. The ΣCO_2 is conservative to mixing, meaning that mixing two samples together in equal measure, one with a typical surface ocean ΣCO_2 concentration of 2,000 micromolar and another with a deep ocean value of 2,200 micromolar, would produce a daughter solution of 2,100 micromolar concentration.

The other derived quantity is the alkalinity of the solution. To recreate the carbonate buffer chemistry of seawater, one would need ingredients of water and CO_2 . One would also need a source of chemical base, something to consume H^+ and allow H_2CO_3 to form HCO_3^- and $\text{CO}_3^{=}$. The amount of base that would be required is equal to the alkalinity. Another way to tabulate it would be to add up the electrical charges carried by the carbonate buffer species:

$$\text{alk}_c = [\text{HCO}_3^-] + 2 [\text{CO}_3^{=}], \quad (7)$$

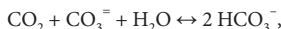
where the factor of 2 before $[\text{CO}_3^{=}]$ is for its -2 charge.

In practice, alkalinity can be precisely measured by doing a pH titration and recording the change in pH resulting from the addition of many small doses of acid. A pH titration measures how much acid is required to bring the solution to a point where all the CO_2 could escape the solution as a gas, called the CO_2 end-point. There are other ions in seawater that will also take up protons if you acidify the solution to the CO_2 endpoint, most notably the couple between boric acid, $\text{B}(\text{OH})_3$, and borate, $\text{B}(\text{OH})_4^-$:



The alkalinity given in equation 7 is called the carbonate alkalinity, to distinguish it from a measurement of total alkalinity as it would be measured in a pH titration. Carbonate alkalinity can be calculated from total alkalinity if you know the total concentration of the borate and other acid-neutralizing species in the solution, generally a simple function of salinity.

Alkalinity has the property of being conservative to mixing, like ΣCO_2 . When two buffer chemistries are merged, finding the new equilibrium will no doubt require some adjustment of the pH chemistry, according to equation 5:



but notice that there are two “equivalents” of alkalinity (a fancy word for “charges”) on the left and two on the right. Shifts back and forth in this reaction do not affect the alkalinity. Alkalinity is also unaffected by the addition and removal of CO_2 gas, even though the addition of CO_2 gas would shift the above reaction to the right.

Alkalinity and total CO_2 are the working variables in many ocean geochemistry models, because they can be advected and mixed like ordinary tracers. When it comes time to calculate whether CO_2 is degassing from the surface ocean, for example, the model needs to know the surface ocean pCO_2 , which it calculates from the model state variables, alkalinity and ΣCO_2 . Let's say that some CO_2 dissolves in the surface water, increasing the ΣCO_2 but leaving alkalinity unchanged. For the next time step the new sea surface pCO_2 is calculated from the new ΣCO_2 and the alkalinity.

The effect of the pH buffer chemistry manifests itself in the way that the surface water pCO_2 changes as CO_2 is added. If the alkalinity and ΣCO_2 are such that the concentration of CO_3^{2-} is high in the surface water, you can add CO_2 (increasing

(Box 3.1 continued)

ΣCO_2 and leaving alkalinity unchanged), then recalculate the effect on the water's pCO_2 , and you will find a relatively small effect. As more CO_2 is absorbed and the $\text{CO}_3^{=}$ concentration declines, the change in pCO_2 of the surface water gets stronger as you add CO_2 .

If $\text{CO}_3^{=}$ drops below the saturation value for CaCO_3 (see box 3.3, "The CaCO_3 Cycle"), then CaCO_3 if present might start to dissolve, releasing $\text{CO}_3^{=}$ into solution. One mole of CaCO_3 dissolved would feed back to the model chemical state as the addition of one mole of ΣCO_2 and two equivalents (= moles) of alkalinity.

Further reading: Stuiver, Quay, and Ostlund 1983; Zeebe and Wolf-Gladrow 2001.

ocean find that if the average temperature of the ocean is changed by 1°C , the CO_2 concentration in the atmosphere changes by about 4%, pretty much in line with the simple homogeneous bucket of seawater.

The temperature of the water in the deep ocean is largely set when the parcel of water was at the sea surface. Water sinks from the surface into the abyss when it is denser than all the rest of the water in the ocean, so the deep ocean is filled with whatever water body achieves the greatest density at the sea surface. The density of seawater depends on its temperature (colder is denser) and salinity (saltier is denser). Warm salty water sinks in the Mediterranean, but the waters that sink to the bottom of the deep ocean are all very cold. The deep ocean is filled with water that last saw the atmosphere in the high

latitudes, either in the marginal seas around Antarctica or in the high North Atlantic.

It is not obvious that the temperature of the deep ocean should change with a change in surface climate. Deep waters usually come from places where there is ice, and the melting temperature of ice did not change between the Last Glacial Maximum and today. But there are proxy estimates of the temperature of the deep ocean during glacial times, and they find that it was actually a few degrees Celsius colder then. The average temperature of the deep ocean today is about 2°C, whereas during glacial times it was about -1°C, very close to the freezing point of seawater, which is about -2°C.

If there is always ice in high-latitude surface waters, during glacial and interglacial times, how can deep waters be colder during glacial times? The deep ocean is filled today by two sources, one in the North Atlantic Ocean, which is warmer than the other in the Southern Ocean around Antarctica. During glacial time there was less deep water formed in the North Atlantic, and it didn't sink as deeply, leaving the deep ocean filled with the colder Southern Ocean water source.

During the last glacial time, the temperature of the deep ocean took a few thousand-year excursions, according to proxy measurements from oxygen isotopes (see box 2.2, "The World According to Oxygen Isotopes") and the concentration of magnesium in deep sea CaCO_3 (figure 5). Atmospheric pCO_2 rose and fell about 20 ppm. Atmospheric CO_2 also decreased during the Little Ice Age by 10 ppm. Both of these covariations of

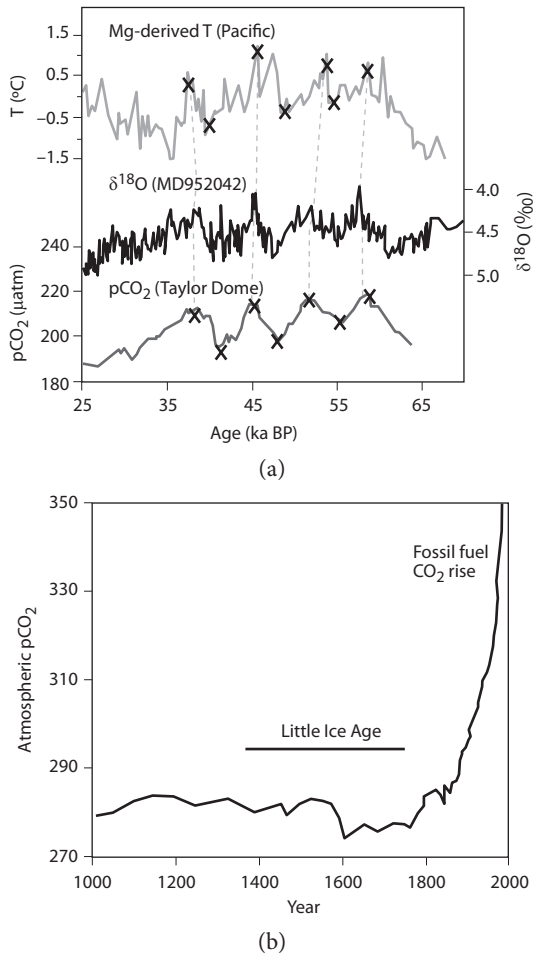


Figure 5. Two cases of apparent atmospheric pCO₂ response to changing temperature in the ocean: (a) during glacial times, and (b) during the Little Ice Age. (Sources: (a) Martin et al. 2005; units of microatmosphere (μatm) are numerically similar to ppm used elsewhere in this book; (b) Archer 2009)

temperature and $p\text{CO}_2$ are consistent with the temperature dependence of CO_2 solubility in seawater (Martin, Archer, and Lea 2005).

It appears that the temperature effect on CO_2 solubility is well enough understood that the largest CO_2 change, the 80 ppm transition from the glacial world to the interglacial, cannot be accounted for just by the temperature effect on solubility alone. The deep ocean warmed at the end of the glacial time by about $2\text{--}3^\circ\text{C}$, enough to drive 20–30 ppm of CO_2 rise, but not the entire 80 ppm.

Changes in Ocean Biology

Plankton in the ocean alter the carbon cycle by taking up CO_2 from surface waters when they do photosynthesis, and then taking the carbon down into the deep ocean when they die and sink. This effect has been dubbed “the biological pump” (see box 3.2, “Biological Pump in the Ocean”).

The net impact of the biological pump is to lower the CO_2 concentration of the atmosphere relative to what it would be if the oceans had no life in them. If the plankton in the ocean were suddenly killed, the CO_2 concentration in the air would rise, on a time scale of a few centuries (the atmosphere–ocean equilibration time), and then subside back to its original CO_2 concentration, as the weathering CO_2 thermostat kicked in over the next few hundreds of thousands of years. Changes in the ocean’s biological pump are one potential mechanism

Box 3.2**Biological Pump in the Ocean**

Dissolved stuff in the ocean, like salt, stays with the water it's dissolved in as it flows around the ocean. But plankton in the ocean are not dissolved. They are particles, and some of them eat particles and secrete waste in the form of particles. Depending on their size and density, particles sink through the waters of the ocean, carrying their elements from one water mass to another. Some of the sinking particles reach the seafloor, but most of them decompose in the water column, releasing their elements back to the dissolved state but pumping it from shallow waters to deep.

Phytoplankton (microscopic algae) produce organic carbon from dissolved CO_2 in the seawater, and when the organic carbon is respired, it releases CO_2 again. How much carbon the phytoplankton can take is usually limited by the availability of nutrients such as nitrate (NO_3^-), phosphate (PO_4^{3-}), or trace elements such as iron. The availability of CO_2 itself is rarely limiting to phytoplankton growth in the long run, but may limit the rate of phytoplankton growth in blooms.

Phytoplankton on average take up carbon and nutrients in a stable molecular ratio, called the Redfield ratio. Because the elements travel together in particles built in this ratio, their dissolved concentrations in seawater covary in this ratio also. The apparent molecular formula for phytoplankton, the classical ratio as Redfield diagnosed it from water chemistry measurements, is $\text{C}_{106}\text{N}_{16}\text{P}_1$. A more recent data analysis finds a slightly higher proportion of carbon, $\text{C}_{125}\text{N}_{16}\text{P}_1$ (Anderson 1994).

The concentration of carbon in seawater is in excess of the nutrients nitrogen and phosphorus, so that high-nutrient waters have about 10% more dissolved total CO_2 than nutrient-depleted waters (see box 3.1, "Carbonate System pH Chemistry"). The

carbon that travels with nutrients through the biological pump, that extra 10%, is called the metabolic carbon.

Some phytoplankton make shells of CaCO_3 or silica (SiO_2), both from dissolved ingredients. These also redissolve in the water column as they sink, but somewhat more slowly than the soft bits (the organic matter). The concentrations of dissolved nutrients tend to be highest in the middle of the water column, while alkalinity (from CaCO_3) and dissolved silica concentrations tend to reach their maxima deeper in the water column.

The net effect of the biological pump is to concentrate the biologically active elements into deeper waters, depleting them at the ocean's surface. Chemicals that limit phytoplankton growth, such as nitrate and phosphate, may be nearly gone in surface waters, while chemicals that are not limiting, such as CO_2 , are slightly lower in the surface but not approaching zero concentration.

Organic carbon production and sinking to depth tends to reduce the CO_2 concentrations and pCO_2 of surface waters by pumping dissolved CO_2 into deep water. The CaCO_3 pump works in the opposite direction, increasing the CO_2 concentration and pCO_2 , by removing $\text{CO}_3^{=}$ from the surface waters (see the box 3.1, "Carbonate System pH Chemistry"). Since more moles of organic carbon sink out of the surface ocean than moles of CaCO_3 (about ten times more), the overall effect of the biological pump is to decrease the CO_2 concentration of surface waters and the atmosphere.

Further reading: Sarmiento and Gruber 2006.

for driving changes in atmospheric pCO_2 over the glacial cycles.

Plankton growth in the ocean is affected by many factors. One is the availability of light, the required energy source for photosynthesis (see box 1.4, "Photosynthesis

and Respiration”). Depending on the intensity of the sunlight and the clarity of the water, there is enough sunlight to support photosynthesis down to a depth of about 100 meters. This depth range is called the euphotic zone.

Another factor is the availability of the fertilizer elements nitrogen, in the forms of nitrate (NO_3^-) and ammonia (NH_4^+), and phosphorus, in the form of phosphate (PO_4^{3-}). In many parts of the surface ocean, the nutrients are basically gone, and the plankton must wait for mixing or fluid flow to bring fresh nutrients up into the euphotic zone from below.

The element iron (Fe) appears to be an essential trace nutrient that limits phytoplankton growth in some places. Iron is an essential ingredient in a few key enzymes, for example the enzyme that converts nitrate (NO_3^-) into ammonia (NH_4^+), the chemical form for making biomolecules such as DNA and proteins. Large stretches of the surface ocean, such as the equatorial Pacific, are replete with sunlight and the major nutrients nitrate and phosphate, but they are biological deserts. When oceanographers add iron to the surface waters, the phytoplankton bloom. The oceanographer who discovered this, John Martin, said that given a tanker full of iron, he could write his name in the surface ocean and read it in satellite maps of ocean chlorophyll concentration (Martin and Gordon 1988).

Iron is quite soluble in anoxic conditions, such as in sediments and in some parts of the water column, like the Black Sea, where it takes the chemical form Fe^{2+} . But the thermodynamically stable form of iron in oxygenated

conditions is Fe^{3+} , which is insoluble in water, tending to precipitate as solid phases, either in tiny suspended particles called colloids or stuck onto some previously existing solid particle. As iron-bearing particles sink, they leave behind an iron deficit in surface waters that can limit phytoplankton production.

Fortunately for the phytoplankton, some Fe^{3+} is stabilized in solution by the action of organic molecules dissolved in the water that bind the Fe^{3+} , recruiting it into a package that is soluble even if the Fe^{3+} by itself would not be (Rue and Bruland 1995). Soap works like this, holding insoluble oils and dirt in solution, allowing them to be washed away. The iron-binding molecules are called chelators or siderophores, and they appear to be biological in origin.

The details of the iron cycle in the ocean are still being worked out, but there is room to think about how changes in iron availability could have had an impact on the glacial carbon cycle. Iron is supplied to the surface ocean in the form of dust, windblown from the continents, and as suspended particles in river water. The glacial world was a dustier place than the interglacial world because of the aridity and higher wind speeds of the glacial climate. A dustier atmosphere could have stimulated the biology of the ocean.

Because of the action of the biological pump, the CO_2 concentration of the deep ocean tends to be higher than the concentration at the surface. The difference between surface and deep-water CO_2 concentrations is determined by the balance between biological particles sinking, which

intensifies the concentration difference, and water circulating and mixing, which smoothes out the concentration differences. Atmospheric CO_2 could be drawn down by stimulating the biology to run faster, or by slowing the rate of mixing, allowing the same biological activity to deplete the surface ocean concentrations more completely.

Could the biological pump have been stronger during glacial times, explaining why the CO_2 concentration in the air was lower? The answer is, maybe a bit. The impact of the biological pump on atmospheric CO_2 is limited first of all by the amount of nutrients in the ocean. If nutrients such as nitrate and phosphate were completely stripped out of surface waters, the strongest possible biological pump, it would be pulling the atmospheric CO_2 concentration as low as it could theoretically go.

Simple models of the ocean carbon cycle initially seemed to indicate that the biological pump could easily pull CO_2 down to 200 ppm or even lower. These models were based on a simple representation of ocean circulation, called box models, where the ocean is represented as a small number of boxes, each of which is considered well mixed, with fluid flow between them.

The atmospheric CO_2 concentration above a more sophisticated type of ocean model, called a general circulation model, or GCM, turned out to be less sensitive to changes in the efficiency of the biological pump (Archer et al. 2000). A GCM represents the ocean flow on a three-dimensional grid, with velocities, temperatures, CO_2 and nutrient concentrations, and so on stored at each grid point. The salient difference to the carbon cycle

between the two model types appears to be in how the models represent the flow of water in the high-latitude surface ocean, the places where surface water becomes dense enough to sink to the abyss.

In a GCM, even if the programmer instructs the model phytoplankton to take up the major nutrients nitrogen and phosphorus as quickly as possible, it still happens that metabolic CO_2 slips out to the atmosphere (Ito 2005). Some of the water at the surface ocean sees the atmosphere for such a brief period that in practical terms, the biological pump can never completely use up the nutrients in the surface waters. The simpler circulation schemes in the box models allow the biological pump to capture the upwelling nutrients and carbon more effectively, preventing the metabolic CO_2 from escaping to the air.

The real ocean is a continuum, which a GCM attempts to simulate, rather than a series of well-mixed reservoirs as in the box models, so the potential impact of the biological pump on pCO_2 is probably in the lower range, like the GCM's, rather than the higher sensitivity predicted by the box models. In my opinion, box models are not to be trusted on the question of the biological pump and atmospheric CO_2 , but they continue to be used because they are easier to set up and manipulate than a full-blown GCM.

There are proxy estimates of the nutrient concentrations of surface waters, for example the concentration of the element cadmium (Cd) in CaCO_3 . These proxies do not show any huge changes in the amount of nutrients in the surface ocean between glacial and interglacial times. There apparently were significant changes in some

regions, such as the sub-Antarctic Ocean. Overall, however, the impact of these surface ocean nutrient changes, indicative of the strength of the biological pump, would have led to an atmospheric CO_2 change that would have been smaller than the 80–100 ppm glacial drawdown we are trying to account for (Brovkin et al. 2007).

It could be that the overall inventory of nutrients in the whole ocean changes through the glacial cycles. The surface concentrations might not be much lower, but the deep concentrations could be higher, the thinking goes, allowing the biological pump to sequester more CO_2 in the deep ocean. One biological role for the element iron is in the machinery for nitrogen fixation, a process that converts the biologically inactive form of nitrogen gas (N_2) into ammonia. The lifetime of nitrate in the ocean is about 10,000 years, more or less, so it's possible that there has been a glacial cycle in the amount of nitrate in the ocean. Unfortunately there are no actual samples of ancient seawater, analogous to the air bubbles in ice cores, to settle the issue.

The biological pump creates oxygen demand in the deep ocean, because when dead plankton decompose, releasing their carbon and nutrients, they consume oxygen. The oxygen concentration of the deep ocean is therefore another indicator for the strength of the biological pump. Without oxygen, multicellular life in the sediment disappears. Their passage through the mud mixes it, and when they are gone the mud accumulates in visible layers like tree rings. For the biological pump to explain the entire CO_2 drawdown, the deep ocean

would have to have been anoxic or close to it—a state easily detectable had it existed.

Anoxia in the ocean would drive a chemical reaction called denitrification, in which nitrate is used for respiration in place of oxygen (Karl 2002). Nitrate, NO_3^- , is the oxidized form of nitrogen, and denitrification reduces it to nitrogen gas, N_2 . Add nitrate to the ocean and the biological pump will get stronger, making more of the deep ocean anoxic, and driving the denitrification reaction to consume nitrate. The nitrate cycle in the ocean seems as though it might be self-limiting, with anoxia tending to limit how much nitrate could build up in the ocean.

The biological pump leaves a signature in carbon isotopes. Photosynthesis preferentially takes up carbon-12 to make isotopically light organic matter with a $\delta^{13}\text{C}$ of about -25‰ . This leaves behind a bit of extra carbon-13 in the surface waters. When this stuff decomposes in the deep water, it makes the isotopic composition of the carbon there a bit isotopically lighter. The efficiency of the biological pump is encoded in the $\delta^{13}\text{C}$ values of CaCO_3 from foraminifera, some shells of which were produced at the sea surface (planktonic) and some on the seafloor (benthic). This carbon isotopic proxy for the biological pump shows that the chemical difference between surface and deep water was a bit stronger during glacial times, not enough to explain the whole CO_2 drawdown but perhaps some of it (Shackleton 1977).

The ocean around Antarctica plays an important role in the biological pump because this is where the water at the surface is the densest, and therefore the

most connected with waters of the abyss. The atmospheric CO_2 is particularly sensitive to changes in the Southern Ocean's surface chemistry, especially in box models, but also in GCMs, and apparently in the real world as well, as evidenced by the correlations among the Southern Ocean's temperature, circulation, and the atmospheric CO_2 concentration. The end of the last ice age was presaged by rising temperatures in Antarctica, followed shortly thereafter by a rise in atmospheric CO_2 concentration.

Antarctica is ringed by a belt of sediments composed mostly of the shells of diatoms, single-celled algae with shells made of silica (SiO_2). The raw material for the silica shells is drawn from seawater, from dissolved silica. Silica concentrations in the ocean resemble those of the nutrients nitrate and phosphate, generally depleted by biology at the surface and in higher concentrations in the deep. Where dissolved silica is abundant in surface waters, diatoms tend to outcompete the other forms of phytoplankton for the available nitrate and phosphate. Diatoms are found throughout the world's ocean, but the high dissolved silica concentrations in the surface waters and the cold bloom-and-bust conditions in the Southern Ocean produce sediments that are different from anywhere else in the world.

During glacial times, the Southern Ocean silica belt moved farther north, and the region of low sediment accumulation next to the Antarctic continent expanded (Franck 2000). Today the boundary of the silica belt corresponds to a boundary in the surface ocean called the

polar front, between cold silica-rich waters to the south and warmer, silica-depleted waters to the north. It could be that the polar front was farther north during glacial times, but the physical oceanographers would prefer that the location of the front be pinned by factors such as the edges of the continents and the bathymetry of the seafloor.

One idea, called the silicate leak hypothesis (Brzezinski 2002), is that iron in dust deposited in the Southern Ocean during glacial times allowed the diatoms to use less silica. It is just an observation that the diatoms use more silica in iron-limited conditions such as we have today; no one knows why, but maybe they did that same thing in response to iron during the glacial time. If dissolved silica was allowed to leak through to the warm side of the front, it would alter the balance of silica to the other nutrients, nitrate and phosphate, in the warmer surface waters of the whole world ocean. More silica could have altered atmospheric CO_2 by shifting the balance between diatoms and other types of phytoplankton, in particular the ones that produce shells of CaCO_3 , the coccolithophorids. Ultimately, a shift in CaCO_3 production could change the pH of the ocean, as is explained below.

There are geochemical indications that the circulation of the Southern Ocean changed during glacial times, manifested in a slowdown in the exchange of water between the surface and the deep water. This conclusion is based on isotopes of nitrogen (Sigman 1999) and silica (De La Rocha 1998), which tell us something about the strength of the biological pump. In particular, the isotopic

ratio is controlled by what fraction of the nitrate in an upwelled parcel of water gets taken up by phytoplankton before the parcel sinks again out of the euphotic zone. Nitrogen and silica isotopes indicate that phytoplankton used a higher fraction of the upwelling nitrate, but sediments were not accumulating any faster. The conclusion is that the Southern Ocean must have been more stagnant during glacial times. The biological pump was more efficient in stripping the upwelling water of nutrients not because biology ran faster but because less water came up from below.

If the efficiency of the biological pump were stronger in the Southern Ocean than it is today, it would pull CO_2 out of the atmosphere—what we're looking for. However, as has already been noted, the carbon isotopes and markers for sediment anoxia both indicate that the biological pump alone cannot explain the entire CO_2 change between glacial and interglacial times, either by fertilizing the plankton or by slowing the circulation. Some of it, perhaps, but not all of it.

Ocean Rearrangement

There are theories for the CO_2 drawdown that are based on the distribution and circulation of the water masses in the deep ocean. The chemical patterns in the Atlantic Ocean are most clearly documented, because sediments of the Atlantic contain the most CaCO_3 (see box 3.3, "The CaCO_3 Cycle"). They show that the boundary between the northern and southern water masses was

Box 3.3**The CaCO_3 Cycle**

There are two main crystalline arrangements for CaCO_3 , called calcite and aragonite. The solubility of either mineral is determined by a saturation state:

$$K'_{\text{sp}} = [\text{Ca}^{2+}] [\text{CO}_3^{=}],$$

where K'_{sp} is an apparent equilibrium constant (see box 3.1, “Carbonate System pH Chemistry”) called a solubility product. The concentrations of Ca^{2+} and $\text{CO}_3^{=}$ need to be in units of moles/liter of solution.

In practice, throughout the ocean, there is so much calcium that reactions with CaCO_3 have relatively little impact on the calcium concentration. The concentration of $\text{CO}_3^{=}$, on the other hand, varies by a factor of 2 from one part of the ocean to another, controlled by the carbonate buffer system chemistry and driven by the cycling of CO_2 in addition to $\text{CO}_3^{=}$. Since the Ca^{2+} concentration is nearly uniform, the solubility for CaCO_3 in seawater is often described in terms of the $\text{CO}_3^{=}$ concentration in equilibrium, CO_3^{sat} .

When CaCO_3 in either form dissolves, there is a slight decrease in volume, so that when you squeeze it, it tends to dissolve more. This means that CO_3^{sat} , the equilibrium concentration in the water, increases as you go deeper in the ocean. The K'_{sp} for aragonite is about 75% higher than the K'_{sp} for calcite, meaning that CO_3^{sat} for aragonite is about 75% higher. The solubilities of the minerals trace similar curves in figure 6.

The biological pump (see box 3.2, “Biological Pump in the Ocean”) decreases the CO_2 concentration of the surface ocean relative to the deep. The patterns of $\text{CO}_3^{=}$ are inverse to those of CO_2 in the ocean, so that the ocean surface tends to have high

(Box 3.3 continued)

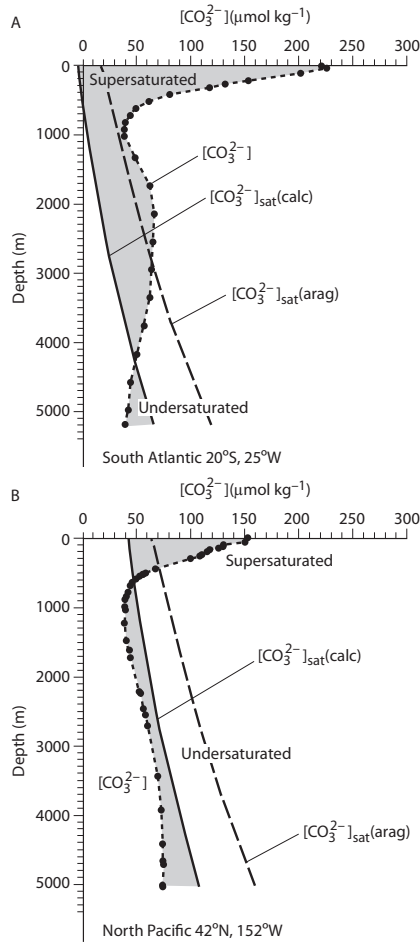


Figure 6. Saturation of CaCO_3 in the ocean.
(Source: Sarmiento and Gruber 2006)

concentrations of $\text{CO}_3^{=}$. For this reason, the CaCO_3 in either mineral form is thermodynamically stable in most surface waters, but when it sinks to the high pressure of the abyss it tends to dissolve.

The transition from supersaturation at the surface to undersaturation at depth is called the "saturation horizon." Aragonite is more soluble than calcite, so the saturation horizon is shallower for aragonite than it is for calcite. Aragonite is found only in very shallow sediments, at a few hundred meters depth generally, while calcite covers a wider swath of the seafloor, to water depths of several kilometers, covering about a quarter of the seafloor area. Sediments that are shallower than the calcite saturation horizon tend to preserve at least some of the calcite that falls to the seafloor, while sediments in deeper waters lose their calcite to dissolution. The distribution of calcite on the seafloor resembles snow-capped peaks, with white carbonate sediments on topographic highs and dark mud in the abyss.

The transition between calcite-abundant and calcite-depleted sediments has been dubbed the calcite compensation depth, or CCD, based on the idea that dissolution is fast enough at that depth to "compensate" for the arrival of new stuff from above. If the saturation horizon is analogous to the freezing altitude in the snow-capped peak analogy, the CCD is analogous to the snow line. When snow falls quickly enough, it accumulates even where the air is a few degrees above freezing. So too the CCD may be a few hundred meters deeper than the saturation horizon.

The depth of the saturation horizon depends on the pH of the water column, in that it is shallower in waters that are more acidic. This is because more of the dissolved carbon is in the form of $\text{CO}_3^{=}$, a building block for CaCO_3 , in base than in acid. The pH of waters in the ocean is affected by fossil fuel invasion, which leads to CaCO_3 dissolution. The biological pump also

(Box 3.3 continued)

affects ocean pH, which becomes more acidic as CO_2 is added from decomposing organic matter. Deep waters in the Pacific are older than they are in the Atlantic, with more metabolic CO_2 , and therefore are more acidic. The saturation horizon is shallower, therefore, in the Pacific than in the Atlantic.

CaCO_3 pH-STAT

The CaCO_3 cycle in the ocean ultimately controls the pH of the ocean. The idea is that removal of CaCO_3 from the ocean, by burial of shells on the seafloor, must eventually balance the rate of addition of CaCO_3 to the ocean by dissolution of CaCO_3 on land (weathering). If the ocean is too acidic, CaCO_3 will dissolve in the acid rather than accumulate on the seafloor, and more dissolved CaCO_3 will enter the ocean than leave it. The acidity will drop as it is neutralized by the antacid CaCO_3 (see box 3.1, “Carbonate System pH Chemistry”). The result of this chemistry is a stable negative-feedback system that regulates the pH of the ocean on time scales of a few thousand years and longer.

shallower during glacial times than it is today. There was a relatively smaller volume of the middle-depth waters that sink in the North Atlantic and relatively more of the really dense waters originating in Antarctica.

Antarctic-origin waters contain more nutrients and metabolic carbon than the North Atlantic-origin waters, so increasing the volume of Antarctic origin water might provide a place to stash carbon during glacial times. This is another ca. 10% effect, able to take up a significant amount of CO_2 , maybe 10–20 ppm in the atmosphere, but

not able to explain the entire glacial CO_2 cycle any more than any of the other ideas we have discussed (Brovkin et al. 2007).

It could be that the chemical stratification of the ocean was more intense in glacial times than it is now. Southern Ocean source waters are generally more isolated from the atmosphere than are waters of North Atlantic origin because of the configuration of the continents and oceans. Antarctica is surrounded by water continuously around the world, which prevents ocean currents on our rotating planet from crossing south to the Antarctic coast. Coastal waters around Antarctica, where the densest water is formed, have to come up from below. North Atlantic deep waters are made from the northward flow of surface water, with plenty of time for air and sunlight to change the chemistry of the water.

There appears to have been a very salty, particularly stagnant blob of water in the deepest Southern Ocean during glacial times (Adkins, McIntyre, and Schrag 2002). Ocean models are able to reproduce this feature if they make enough sea ice in Antarctica that the winds blow ice out of the Antarctic region (Shin et al. 2003). The ice is made of freshwater, and when it is removed, the salt it left behind accumulates in a water mass I have always thought of as the deep salty blob. Perhaps this is where the missing carbon can go during glacial times.

How much carbon can we put in the blob, and what impact would that have on atmospheric CO_2 ? The deep-sea pore-water data say that the blob could have had a salinity of 37 grams/liter, at most, say, 10% higher than

the ocean average of about 35 grams/liter. If we assign the blob 10% of the volume of the ocean and give it 10% higher concentrations of all the dissolved stuff in the water, including the carbon, then we end up storing about 400 Gton C in the blob. This is over and above the carbon that would have been there if the salinity had been average.

The atmospheric drawdown to making a salty blob in this way would be very small, because most of the carbon in seawater is in the form of bicarbonate rather than CO_2 . If, hypothetically, the carbon were somehow removed in the form of CO_2 , after a few thousand years (after equilibration of the ocean pH-stat) the airborne fraction would be about 10%, changing atmospheric pCO_2 by about 20 ppm (see box 4.3, “Airborne Fraction of a CO_2 Slug over Geologic Time”). Removing carbon by concentrating seawater, taking the carbon mostly as bicarbonate, would have had almost no impact.

It could be that the blob water is stagnant because of the salt, but the carbon gets into the blob as sinking particles rather than as part of the salt. The carbon-13 values of benthic foraminifera from the glacial Southern Ocean are extremely low (Hodell 2005), so low that many paleo-oceanographers consider them an artifact of the way that the foraminifera get their carbon to make shells in areas of high organic carbon rain to the seafloor (Mackensen 1996). There are uranium minerals found in glacial Antarctic sediments that today form only in very low-oxygen or very productive environments (Chase 2001).

In the ocean today, there are waters with nutrient concentrations much below the average ocean value, but not too many waters with much higher than average nutrient concentrations. This is because nutrients get used up in the shallow surface ocean, resulting in low and variable concentrations, whereas the high nutrient concentrations are found in the deep ocean, in which the chemistry is more homogeneous. However, let's imagine that the concentration of nutrients in the deep salty blob was twice the ocean average. Doubling the metabolic carbon concentration would result in about 10% more total CO_2 than the average deep-ocean water has today. Crunching the numbers, if the blob filled 10% of the ocean, we could imagine putting about 500 Gton C in it. The airborne fraction of this CO_2 (after the CaCO_3 pH-stat) would be 10% (see box 4.3, "Airborne fraction of a CO_2 Slug over Geologic Time"), leaving 50 Gton C or 25 ppm in the atmosphere. However, any buildup of alkalinity in the blob by dissolution of CaCO_3 would tend to reduce the atmospheric pCO_2 drawdown.

If we wanted a single explanation for the glacial CO_2 cycles, we'd probably look for a carbon sink about four times the size of this. Since our estimate was based on an extreme scenario, doubling the nutrient concentration of the blob water, we can conclude that the blob nutrient hypothesis is potentially significant but that it can't explain the entire CO_2 drawdown during glacial time any more than the other hypotheses discussed.



Changes in Ocean pH

Perhaps the glacial world hid the carbon as bicarbonate dissolved in seawater. Seawater has 100 times more bicarbonate than dissolved CO_2 . Changing the balance between CO_2 and bicarbonate would require a change in ocean pH, which is controlled by the CaCO_3 cycle pH-stat. It might be useful here to review box 3.1, “Carbonate System pH Chemistry,” and box 3.3, “The CaCO_3 Cycle.”

One possibility would be to increase the rate of weathering of CaCO_3 on land. With all else held constant, more dissolved CaCO_3 flowing into the ocean would drive up ocean pH until CaCO_3 accumulated more quickly on the seafloor to keep pace. Did this happen? The best indication, the most direct measurement, would be to see more CaCO_3 accumulating on the seafloor during glacial time (see box 3.3, “The CaCO_3 Cycle”). There are a few places on the seafloor with clear increases in CaCO_3 burial during glacial times, but overall there’s no convincing evidence that the global burial rate of CaCO_3 in the deep sea was much different than it is today.

Another theory for lowering glacial atmospheric CO_2 via pH is called the coral reef hypothesis, which proposes that CaCO_3 depositing in shallow waters today moved to the deep sea during glacial times (Berger and Keir 1984). Today, lots of CaCO_3 accumulates in shallow waters on the continental shelves. Lowered sea levels during glacial times left most of that area high and dry, subject to erosion instead of sedimentation. Deprived of shallow-water sediments, the ocean might have needed a higher

pH to bury enough CaCO_3 in the deep sea to balance the influx from weathering.

The coral reef hypothesis is undermined by the same observation that torpedoed the increased CaCO_3 weathering idea; the global burial rate of CaCO_3 in the deep ocean was not very different during glacial times than it is today. That doesn't mean that the ideas are wrong, but it limits how much CO_2 drawdown can be explained by these mechanisms to maybe 10–20 ppm or so, a fraction of the total drawdown. Where have we heard that before?

The distribution of CO_2 in the ocean might affect the setting of the pH-stat (Boyle 1988). Nutrients in the ocean travel with metabolic CO_2 (see box 3.3, "Biological Pump in the Ocean"), and the concentrations of both are generally higher near the seafloor during glacial times. Deep water from Antarctica is high in CO_2 , and it covered more of the seafloor during glacial times. The deep salty blob might have been particularly acidic. Putting CO_2 near the seafloor prevents CaCO_3 from accumulating, and the CaCO_3 pH-stat would have responded by raising the pH of the ocean. Again, however, the potential CO_2 drawdown from this mechanism appears to be too small to explain the entire drawdown.

The burial of CaCO_3 on the seafloor may depend on the balance of organic carbon and CaCO_3 , called the rain ratio, of the sinking particles that land on the seafloor (Archer and Maier-Reimer 1994). Organic carbon when it decomposes releases CO_2 , an acid that causes CaCO_3 to dissolve. Models of the ocean carbon cycle predict that a change in the ratio of organic carbon to CaCO_3 hitting

the seafloor could ultimately drive a change in ocean pH, affecting atmospheric CO_2 .

The change in the rain ratio could have resulted from a change in the ecological balance of the plankton. To lower atmospheric CO_2 , we need fewer plankton that make shells of CaCO_3 . One potential cause is the cooler temperatures of the glacial world. Most geologists associate CaCO_3 sediments with the tropics, and there is no CaCO_3 production at all below about 10°C . Putting these systematics of the CaCO_3 cycle into a carbon cycle model, however, doesn't change atmospheric CO_2 very much (Brovkin et al. 2007).

Another possibility is that there was more silica in surface waters during glacial time, giving the silica-shelled diatoms a competitive advantage. One idea mentioned above, called the silicate leak hypothesis, is that changes in the biology and circulation of the Southern Ocean around Antarctica changed the balance of dissolved silica and nitrate, NO_3^- , in waters of the thermocline.

However, while the ratio of SiO_2 to NO_3^- differs between the surface waters of the Atlantic and the Pacific Ocean today, there isn't a clear difference in the rain ratio of the particles sinking to the seafloor between the two oceans (Honjo 1996). It makes such good sense that more silica should decrease CaCO_3 production that it's hard to imagine why the real phytoplankton haven't thought of it.

It could be that particles that sink to the seafloor would always have the same balance of organic carbon to CaCO_3 , regardless of the composition of the phytoplankton (Armstrong et al. 2002). The idea is that organic

carbon acts as a glue that holds the particle together, making it large enough to sink, and the CaCO_3 acts as ballast, also necessary for sinking. Either constituent without the other would remain suspended in the water column and dissolve in place rather than sinking, this idea goes.

A large change in ocean pH would probably leave CaCO_3 preserved at greater depths in the ocean (see box 3.3, “The CaCO_3 Cycle”), that are not found in sediment cores. There are also paleo-pH proxies based on the chemistries (Honisch 2008) or sizes of CaCO_3 shells buried in sediments (Anderson and Archer 2002; Broecker 2003). These estimates do not always agree with each other very well, but they don’t in general seem to support a huge change in ocean pH during glacial time.

BRINGING IT HOME TO GLOBAL WARMING

At the end of a chapter that has probably been fairly heavy going, the alert reader will have surmised that there is no single satisfactory explanation for the positive ocean carbon cycle feedback responsible for the glacial and interglacial atmospheric CO_2 cycles. The CO_2 that was not in the atmosphere during glacial times must have been in inorganic form in the ocean, the carbon isotopes tell us. We have several potential explanations, none of which suffices to explain the entire CO_2 change. We are left to compose an explanation out of a composite of several different mechanisms, combined together one on top of the other. It is unsettling, because the feedbacks all have to go in the same direction and because the relationship

among ice volume, global temperature, and CO_2 (see figure 4) is so reproducible, so solid.

The unfortunate implication of our ignorance is that we are unable to predict how the ocean carbon cycle will eventually respond to the provocation of our fossil fuel CO_2 release. Some of the proposed mechanisms to explain the past, such as the temperature dependence on CO_2 solubility, would extend in the warming direction, continuing to raise atmospheric CO_2 as the temperatures rise beyond the warmest temperatures of the natural interglacial intervals. If on the other hand the explanation were that the ocean shifted to higher pH in response to the cold climate, it seems plausible but not at all certain that it could shift slowly toward the acidic in a warmer world, driving CO_2 into the atmosphere.

Some of the mechanisms, such as the deep salty blob, may only work in the cold direction, so that warming would not produce some sort of anti-blob that would release CO_2 . Also, there could be carbon cycle changes in the future, such as decomposing frozen peats or methane hydrates, which played no major role in the glacial cycles. (Pop quiz: How do we know that peats and hydrates didn't drive the glacial CO_2 cycle? A: The carbon isotopes tell us that there was less organic carbon, including peats and methane, stored during glacial times, not more, as would be needed to draw down atmospheric CO_2 .)

At present, however, and presumably for the near-term future, the carbon cycle has been acting to stabilize the Earth against human climate forcing by absorbing fossil fuel CO_2 , as described in the next chapter.

4 THE PRESENT AND FUTURE CARBON CYCLE—STABLE OR UNSTABLE?

The carbon cycle at present is acting to dampen the climate change from fossil fuel CO₂ by absorbing the fossil carbon into the ocean and the land biosphere. There are reasons to fear that on longer time scales (say, by the end of the twenty-first century), warming may drive carbon out of soils and the oceans into the atmosphere, amplifying the climate change directly caused by human CO₂ release.

THE CARBON CYCLE TODAY

The Setting

Our interglacial period is called the Holocene. It began about 10,000 years ago. For the most part the carbon cycle has been stable in its Holocene state, although there has been some slow evolution and adjustments. Many Earth scientists refer to the time since the year 1750 as the “Anthropocene,” acknowledging our controlling role in the carbon and other geochemical cycles.

The Earth was probably warmer in the early Holocene than it is today because of the different orbital trajectory

of the Earth around the sun. Interestingly, the Earth's orbit today is very close to what it was during the Last Glacial Maximum, demonstrating that the Earth's climate does not respond to the orbit in a simple, linear way. With lowered CO_2 concentration and lots of shiny ice to reflect sunlight back into space, the glacial climate stabilized its own existence. The climate today is warmer than it was then because of an intervening time of "warm" orbit that drove the Laurentide and Fennoscandian ice sheets to collapse (Paillard 2001).

The pCO_2 of the atmosphere has risen slowly through the Holocene, from 260 ppm 10,000 years ago to 280 ppm in the year 1750. The rise in atmospheric CO_2 concentration is slow enough that the CaCO_3 pH-stat of the ocean must be playing a role. It could be that the CO_2 rise was due to the flooding of the continental shelves when sea levels rose. The extra CaCO_3 burial would have perturbed the CaCO_3 pH-stat, driving the ocean toward the acidic (Kleinen et al. in press).

If anything, the land biosphere has probably gained weight through the interglacial time, which is the wrong direction to explain the Holocene rise in atmospheric CO_2 . The melted ice sheets uncovered much of the land area where peat deposits have since begun accumulating. Today, peats account for at least a quarter of the carbon on land. Peats are swamp deposits, mostly the remains of moss called sphagnum. The land area in which sphagnum grew can be reconstructed from pollen deposits in lake sediments. According to the pollen records, there wasn't nearly as much sphagnum pollen in the air during

the early Holocene, so presumably there was less peat deposition at that time (Gajewski 2001).

The Perturbation

Humans are emitting CO_2 into the atmosphere at a rate of about 10 Gton C per year (see box 4.1, “Human Carbon Emissions”). This is mostly a carbon flux from the solid Earth, from combustion of fossil fuels and cement manufacture, supplemented by the destruction of carbon biomass on land. Our carbon emissions are 100 times larger than the analogous natural carbon flux from the solid Earth to the atmosphere, the degassing of CO_2 in volcanic gases and deep sea hot spring fluids. The human-associated emission rate is growing faster than even the most pessimistic business-as-usual projection, an aggressive growth scenario called A1F1 (Le Quere 2009).

The CO_2 concentration in the air is measured every day in a few dozen locations around the world (figure 8 shows the longest record, from Mauna Loa, Hawaii). There is a seasonal cycle, with CO_2 dropping in the summer owing to plant growth and rising in the winter as plant matter decomposes back to CO_2 . The seasons are out of phase between the hemispheres, and as a result, so also is the CO_2 concentration. The cycle is stronger in the Northern Hemisphere because there is more land surface in the north, the same accident of plate tectonics that allows the north to dominate the glacial climate cycles.

There is also a rising trend in atmospheric CO_2 from human CO_2 emission. There is no doubt about its human

Box 4.1**Human Carbon Emissions**

Most of the carbon we emit is a by-product of the extraction of energy from fossil fuels. Fossil fuel carbon comes in three basic varieties: coal, oil, and gas (see box 1.6, “Origins and Inventories of Fossil Fuels”). Coal is the most abundant of the fossil fuels, and the future of the Earth’s climate will be primarily determined by the fate of coal.

Coal and oil are each being burned at a rate of about 3 Gton C per year, while gas is being consumed at about half that rate, 1.5 Gton C per year. Business-as-usual projections for the coming century predict a shift toward coal as oil and gas become depleted. Fossil fuel energy is used throughout a wide range of human activity and practice. Transportation, electricity, heating and cooling, and industry all account for about an equal share of CO₂ emissions (figure 9) (Le Quere 2009).

Historically, most of the fossil fuel CO₂ emission came from the industrialized nations, but emissions are increasing rapidly in China and India and are overtaking emissions from the developed world through sheer force of numbers of people. The global rate of CO₂ emission from fossil fuel combustion is about 8.5 Gton C per year and is growing by 3% per year. Thus, the global rate is projected to double under business-as-usual scenarios by around 2050.

Humans have also released carbon from the land surface by cutting down trees for agriculture. An old-growth forest holds more carbon per acre than does an agricultural field. The old-growth forest is breathing CO₂ in and out through the seasons, but on average, it is neither a net source nor a sink of CO₂; it is in balance. Cutting down trees and allowing the organic carbon in the soil to decompose releases CO₂ to the atmosphere. Today, deforestation is mostly a tropical phenomenon. The

THE PRESENT AND FUTURE CARBON CYCLE

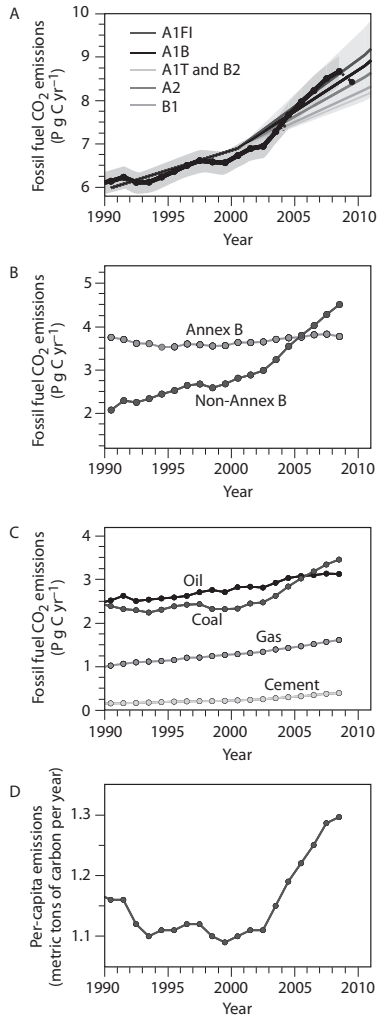


Figure 7. History of CO₂ emissions. (Source: Le Quere 2009)

(Box 4.1 continued)

temperate latitudes were deforested centuries ago, and now there is forest regrowth, driven by the agricultural revolution, which increased the efficiency and decreased the footprint of farming.

Satellite images are used to estimate rates of deforestation, but images from space can't see most of the carbon, which is in the soils. The deforestation carbon flux is a small signal to look for; a few Gton C per year of carbon is less than 1% of the carbon inventory of the living biosphere (the trees, mostly), or about 0.1% of the carbon in soils. The best estimate of the deforestation carbon flux is about 1.5 Gton C per year.

The total human load on the carbon cycle is about 10 Gton C per year. This load comes from fuels, deforestation, and other secondary sources such as the manufacture of cement. This is smaller than the large-scale carbon exchange fluxes in the biosphere, gas exchange with the ocean, and photosynthesis/respiration with ocean and land biota, each of which comes to about 100 Gton C per year. This means that the natural carbon cycle is capable of responding to our perturbation of it in a big way.

However, the closest real analog to the fossil fuel CO₂ release is the natural rate of CO₂ degassing from the solid Earth, which is only about 0.1 Gton C per year, 100 times smaller than human CO₂ release. Both of these fluxes take CO₂ from the solid Earth and add it to the atmosphere-ocean carbon cycle. The human CO₂ release far outpaces weathering, which is why the CO₂ inventory of the atmosphere-ocean-land surface carbon cycle will build up, until weathering can slowly take it back to the solid Earth. Natural degassing is also thought to have been in balance with weathering in the natural carbon cycle, on average over a few million years.

In total, humankind has released about 350 Gton C into the air from fossil fuel combustion. Deforestation has released another 200 Gton C, but the land carbon sink has soaked up about as much carbon as deforestation has released, leaving the land surface, integrated over the human era, roughly carbon neutral in total.

origins. Fossil fuel consists of organic carbon with its characteristically light $\delta^{13}\text{C}$ value of about -25‰ , and it was first formed from photosynthesis of atmospheric CO_2 millions of years ago, so that all of the carbon-14 has decayed away (it is radiocarbon dead). Both of these

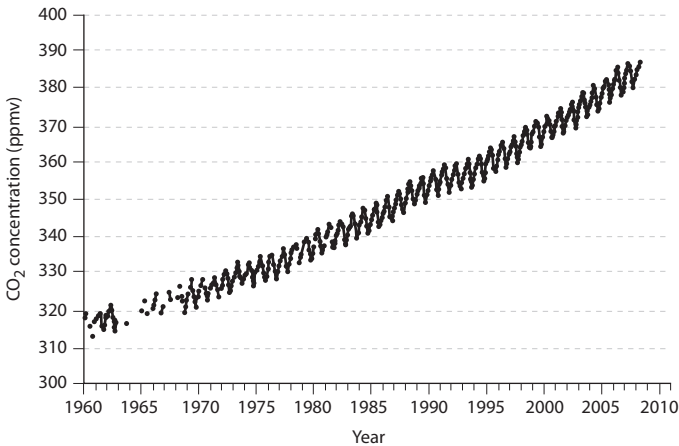


Figure 8. Atmospheric CO_2 concentration measured at Mauna Loa, Hawaii. The unit ppmv is very similar to ppm used elsewhere in this book.

signatures are apparent in changes in the $\delta^{13}\text{C}$ and $\delta^{14}\text{C}$ of CO_2 in the atmosphere (Denman et al. 2006).

The concentration is rising by about 2 ppm/year on average. Remembering the handy factor-of-two conversion between ppm in our atmosphere and Gton C, this rate of concentration increase represents about 4 Gton C per year. This is less than half the rate of the human emission of CO_2 , so there is no problem accounting for where the CO_2 comes from. Instead, we face the issue of figuring out where the rest of the fossil fuel carbon is going. There are two possibilities: carbon can go into the land biosphere or it can go into the ocean.

It is much easier to measure the rate at which fossil fuel CO_2 is being dissolved in the ocean than it is to measure land uptake. The chemistry of the ocean is smoother, more homogeneous, so that a curtain or “transect” of measurements (from a range of depths along a ship cruise track) can reveal smooth large-scale patterns in temperature, chemical concentrations, and so forth. The land surface, in contrast, is extremely heterogeneous. To measure a trend in the amount of carbon in all the soils on Earth would require an almost unimaginable number of soil carbon measurements.

Ocean Uptake

The most direct way to measure the flux of fossil fuel CO_2 dissolving in the ocean is to make lots of measurements of the chemistry of the surface ocean. As described in box 4.2, “Air-Sea Exchange of CO_2 Gas,” the CO_2 flux at

Box 4.2**Air-Sea Exchange of CO₂ Gas**

The rate at which CO₂ dissolves into the surface ocean or evaporates from it depends on the extent of chemical disequilibrium between the air and the water; if they were in equilibrium, the net flux would be zero. The net flux is a slight imbalance between much larger upward and downward fluxes that go on even where the air and water pCO₂ values are equal, and the net flux goes to zero. Today, the global net flux of fossil fuel CO₂ into the oceans is about 2 Gton C per year, amid exchange fluxes of roughly 90 Gton C per year.

The gas flux depends on turbulence and bubbles in the water, which depend on the wind speed. All of this no doubt fiendishly complicated physics is collapsed into an empirical multiplier K_{piston} in the gas exchange equation

$$\text{Gas flux} = K_{\text{piston}} \cdot K'_H{}^{-1} \times (p\text{CO}_2^{\text{air}} - p\text{CO}_2^{\text{water}}),$$

where K_H is Henry's law gas solubility (strictly speaking it should be the apparent constant, denoted with a prime), converting units of pressure (pCO₂) to concentration of H₂CO₃* (moles per volume) (see box 3.1, "Carbonate System pH Chemistry"). The units of the gas flux are moles of CO₂ per surface area per time. To make this work out, the units of K_{piston} have to be length per time, for example, meters/day, and for this reason K_{piston} is called a "piston velocity." A typical piston velocity for the sea surface is about 3 meters/day, so that a water column of 100 meters depth would equilibrate on a time scale of about 33 days, about a month.

The buffer chemistry allows seawater to hold about ten times more CO₂ than it would if the gas was unbuffered. Adding CO₂ doesn't change the H₂CO₃* concentration as much as the amount of the added CO₂, because most of the CO₂ reacts

(Box 4.2 continued)

with $\text{CO}_3^{=}$ in the carbonate buffer system (see box 3.1, “Carbonate System pH Chemistry”). Because of the buffer, it takes ten times longer for the pCO_2 of the ocean to equilibrate than it would for an unbuffered gas. A 100-meter-deep column of seawater, with a piston velocity of 3 meters/day, would approach equilibrium on a time scale of about 330 days, almost a year.

Models of the ocean circulation and carbon cycle predict that CO_2 equilibrates between the atmosphere and the ocean overall on a time scale of a few centuries. From the gas exchange kinetics alone, one might expect an equilibration time scale much shorter than that. A piston velocity of 3 meters/day, combined with the buffer factor of 10 and 4,000 meters water depth, gives an equilibration times scale of 13,000 days, about thirty-five years. The real deep ocean ventilates more slowly than this because of the slowly overturning circulation carrying ventilated surface waters into the abyss.

The functional difference between the large exchange fluxes and the slower uptake fluxes makes it potentially confusing to think about the atmospheric lifetime of CO_2 . The expected lifetime of a particular CO_2 molecule in the atmosphere can be calculated as

$$\begin{aligned}\text{lifetime [years]} &= \text{inventory [Gton C]} / \text{flux [Gton C/yr]} \\ &= 700 \text{ Gton C} / 210 \text{ Gton C yr}^{-1} = 3.5 \text{ years},\end{aligned}$$

where 200 Gton C per year is the combined rates of carbon exchange with the ocean and photosynthesis on land (120 Gton C yr^{-1}). After a CO_2 molecule is released to the air, it will float around for about 3.5 years before it dissolves in water or gets taken up into a leaf. But these are exchange fluxes, where one carbon is exchanged for another, which has no effect on the amount of CO_2 in the air.

To estimate the time it should take for CO₂ to actually move from one reservoir to another, we use the net flux instead of the exchange flux to get

lifetime = inventory/flux = 200 Gton C/2 Gton C yr⁻¹ = 100 years,

which is a more reasonable estimate of the fossil fuel CO₂ uptake time scale into the ocean. But the ocean uptake slows as the buffer chemistry of the ocean changes, ultimately leaving some of the CO₂ in the atmosphere for the duration of the long tail (see box 4.3, “Airborne Fraction of a CO₂ Slug over Geologic Time”).

Further reading: Broecker and Peng 1982.

any time and place depends on how much CO₂ is dissolved in the water relative to the amount that the water would like to hold in equilibrium. Put another way, it is the difference in the pCO₂ between the air and the water.

There is considerable uncertainty, perhaps ±50%, in the exchange rate, even if the chemical concentrations and the wind speed were known perfectly. And then it is even more challenging to average the estimates from all seasons, all around the world, to get the global total net invasion of CO₂ into the ocean. There are huge variations in the pCO₂ of surface waters around the world, driven by temperatures and plankton growth.

To drive the ocean to take up 1 Gton C per year as CO₂ would require that the global average surface ocean pCO₂ be about 2 ppm lower than the pCO₂ of the atmosphere. This means that the average pCO₂ of the surface ocean has to be known within just a few tenths of a ppm in order

to get the global CO_2 invasion flux into the ocean. The pCO_2 of the surface ocean is wildly variable, ranging from 250 ppm in some locations and seasons up to 500 ppm in others. The atmospheric value is currently about 390 ppm, varying with a seasonal cycle of 10 ppm in some places. In some locations there is a net CO_2 flux dissolving into the oceans; in others, there is net CO_2 degassing.

Overall, the back-and-forth exchange fluxes of CO_2 between the atmosphere and the ocean are about 90 Gton C per year, and the fossil fuel invasion introduces just a slight imbalance in these fluxes. Millions of measurements taken by oceanographic research cruises, survey cruises, and ships of opportunity have gone into estimating the rate of fossil fuel invasion into the ocean to be about 2 Gton C per year CO_2 net invasion of the ocean from the land (Takahashi 2009).

Computer models of the circulation and biology of the ocean can be used to estimate fossil fuel uptake into the ocean by simulating the processes that control it—currents, biology, and the resulting chemical concentrations in the ocean. The models, subjected to a rise in atmospheric CO_2 concentration, tend to predict about the same CO_2 uptake rates as the various forms of measurement such as described above (Denman et al. 2006). This is reassuring, although it's a pretty tough problem to capture from first principles in a numerical model. Small-scale mixing in the ocean, for example, is very difficult to understand and model but probably controls the ocean circulation, setting the stage for everything. Plankton ecology seems vastly more complex than the biological

models currently available to represent it. The ocean carbon cycle models do a great job of simulating the present-day invasion of CO_2 into the ocean, but we should not feel too confident in our predictions for the future of the ocean carbon cycle.

Anthropogenic CO_2 can also be detected in the subsurface ocean, but it's tricky because the fossil fuel CO_2 is only a small part of all the carbon dissolved in the ocean. The ocean contains 38,000 Gton C (see box 1.6, "Origins and Inventories of Fossil Fuels"), compared to about 550 Gton C from fossil fuel combustion and deforestation already released (see box 4.1, "Human Carbon Emissions"). About 200 Gton C remains in the atmosphere, so at most, the anthropogenic carbon in the ocean could be about 1% of the natural carbon that was already there (Sabine 2004).

Uptake in the deep ocean depends on ocean currents and mixing, which can be worked out using measurements of chemicals such as freons and tritium. Freon is an artificial class of molecules, entirely man-made, with zero concentration in the atmosphere before it was invented in 1928. Freons are responsible for ozone depletion in the stratosphere, in particular the ozone hole over Antarctica, and are now regulated by the Montreal Protocol. They are also powerful greenhouse gases. Tritium was produced in nuclear bomb tests, mostly in the 1960s, and quickly rained out to the surface ocean in water molecules. High concentrations of these tracers in a subsurface water parcel indicate that the parcel, or some fraction of it, was exposed to the atmosphere sometime in the past decades. Until recently, the atmospheric concentration of freons

rose with time, so the concentration in the water parcel tells something about how much time has passed since the parcel was at the surface (Broecker and Peng 1982).

If the ocean had no biology in it, one could measure the concentration of fossil fuel carbon by comparing the chemistry of one particular water parcel with others that are older or younger. The younger ones would have more CO_2 because there is more fossil fuel CO_2 in the air more recently. Biology in the ocean complicates the calculation, because the plankton are taking up CO_2 in photosynthesis in the surface ocean, and their remains settle and decompose, releasing CO_2 in subsurface waters (see box 3.2, “Biological Pump in the Ocean”). Older waters will have accumulated more “metabolic” CO_2 than younger waters, extra CO_2 that has nothing to do with human activity. The CO_2 concentration measurements can be corrected for biological effects using concentrations of nutrient elements such as nitrogen and phosphorus. These calculations are not trivial, and the state of the art represents many generations of scientific papers (Denman et al. 2006).

The bottom line is that the oceans in the mid-1990s had taken up about 180 Gton C, or about a third of all human-released carbon. Every year the ocean takes up about 2 Gton C, accounting for about a third of the uptake of human-released carbon by the natural world.

Land Uptake

Deforestation converts organic carbon from biomass and soils into CO_2 added to the atmosphere. This represents a

significant fraction of the human CO_2 release, about 1.5 Gton C per year, compared with fossil fuel combustion, at about 8.5 Gton C per year (see box 4.1, “Human Carbon Emissions”).

In order to balance the year-to-year carbon budget, we need a carbon sink on land, some change in the land carbon cycle other than deforestation, which has been called the missing sink. The missing sink is sized by difference of the other known fluxes: if it's emitted but it's not in the atmosphere or the ocean, it must be on land.

Uptake into the land biosphere differs from dissolution in the ocean in that the photosynthesis that drives land uptake releases oxygen gas (O_2) to the atmosphere, whereas CO_2 dissolving in the ocean does not. The concentration of oxygen is decreasing very slightly, owing to the combustion of fossil fuel organic carbon (see box 1.4, “Photosynthesis and Respiration”). But some of this decrease is offset by the oxygen released by of the increase in biological and organic carbon on land. The oxygen and CO_2 results are consistent with the other estimates, with 2 Gton C per year net uptake on land and 2 Gton C per year into the ocean (Keeling, Piper, and Heinman 1996).

A reconstruction of the history of carbon fluxes is shown in figure 9. In the early part of the industrial period, deforestation outpaced any natural land sink, driving atmospheric CO_2 slowly upward until about 1950. In the last fifty years the natural carbon sink has kicked in, taking up enough carbon to bring the land surface, overall, back to a balance of zero net emissions. In the last few

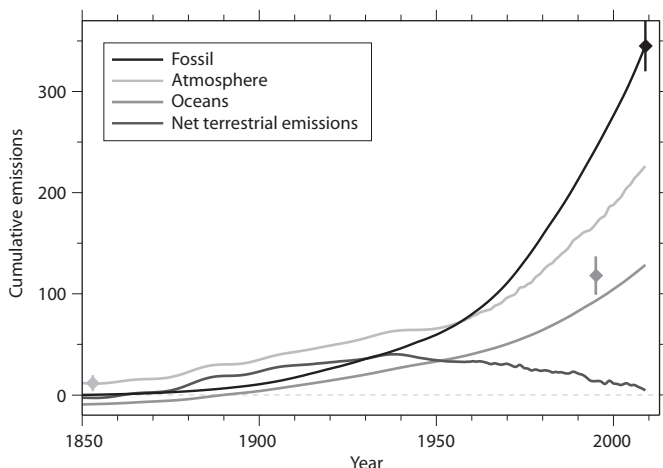


Figure 9. History of CO₂ fluxes. Units: Gton C. (Source: Tans 2009).

years it appears as though the land surface overall has provided a net sink of 1–2 Gton C per year.

But it has proven impossible so far to actually lay hands on this carbon. A gigaton of carbon is a lot of stuff. The entire mass of humankind, not just our carbon but water and bones and all, comes to maybe 0.5 Gton. It's rather amazing that all this stuff can disappear without a trace every year. Much of it is probably hiding within all the heterogeneity of the soil organic carbon pool.

One way to look for the missing carbon is to analyze the variations in CO₂ concentration in the atmosphere around the globe. The data are carefully cross-calibrated so that slight differences in concentrations from one location to another, or one time to another, are meaningful. The data are analyzed in the context of models of

atmospheric circulation (the weather). If the Siberian tundra is a carbon sink because a longer growing season allows shrubs to take hold, then the CO_2 concentration in the air will decrease a bit as the winds blow over Siberia. These “atmospheric inversions” generally (but not always) find the missing carbon in the northern high latitudes (Gurney 2002).

It is possible to estimate the flux of CO_2 going into or coming out of the land surface by measuring the variations in CO_2 concentration on a tower, second by second, along with measurements of the vertical wind direction. If the puffs of air blowing downward carry more CO_2 than the upward-flowing air, then the land surface must be taking up CO_2 . This is called an eddy correlation method (Baldocchi 1996). The method averages the carbon fluxes over some area: the taller the tower the broader the footprint. The measurements can be used to understand better the processes that might be controlling the land carbon uptake, but so far it has not been possible to scale this type of measurement up to global coverage.

One potential cause of the terrestrial uptake is a CO_2 fertilization effect, which stimulates plants to grow faster or larger in a high- CO_2 atmosphere. Greenhouses owe much of their magic to elevated CO_2 concentrations in the air inside them, maintained perhaps by respiration of the organic carbon in the rich soils. Leaf photosynthesis takes place behind a waxy seal, with gas ports called stomata that can be actively opened and closed. The penalty for opening the stomata is the loss

of water as vapor. If the CO_2 concentration in the air is higher, the plants can accomplish their business without losing as much water. The enzyme responsible for CO_2 uptake, called rubisco, also runs more quickly at higher CO_2 concentrations.

Plant growth experiments can be done in the laboratory, but it's not clear how applicable the results of a lab experiment are to the real world. Forestry scientists are taking the experiment into the real world by adding CO_2 to the air upstream of a grove of trees from a ring of towers around the grove. Trees subjected to elevated CO_2 concentrations are found to grow more quickly, but it's not at all clear that they will store more carbon in the end (Lichter 2008; Norby 2002).

Computer models have been constructed of the land surface that predict the types of vegetative cover (pines versus deciduous trees versus tundra, etc.) and the carbon stored per acre. The model variables evolve through time in response to changes in rainfall and temperature and atmospheric CO_2 concentration (Cramer et al. 2001). They balance the potential rates of photosynthesis against the demands of the environment, such as competition between plant types for sunlight, and dealing with water stress. In general, the models work pretty well, reproducing past changes in land biomes with changes in climate. The current generation of land carbon cycle models predicts stronger growth under higher CO_2 conditions, but the latest models, which include the effects of nitrogen limitation, predict a weaker CO_2 fertilization effect.

Other potential mechanisms to explain the mysterious terrestrial carbon uptake include a longer growing season as the climate warms, especially in high latitudes. It could be reforestation, driven by the agricultural revolution increasing crop yields, allowing former farmland to return to forest. Or it could be that nitrate, NO_3^- , in acid rain is fertilizing the plants. Maybe fire suppression in managed “natural” forests is allowing soil and litter carbon stocks to build up.

In the end, we know the rate of carbon uptake by the land surface by the difference between other carbon fluxes that are known better: human emission and ocean invasion. Neither the mechanism nor the location of the missing carbon is known for sure. It will be useful to figure out the real mechanism driving the carbon uptake because it determines how the land will interact with the carbon cycle in the future.

THE FUTURE OF THE CARBON CYCLE

Over millions of years, the carbon cycle acts to stabilize and regulate climate. Changes in the geometry of the Earth's surface, driven by plate tectonics, push the “set-point” of the CO_2 thermostat up and down, allowing Earth's climate to drift slowly from hothouse to icy states. But the carbon cycle is functioning as a regulator of climate, a stabilizing negative feedback.

On glacial cycle time scales of tens of thousands of years, the character of the carbon cycle has changed to that of a climate amplifier. The orbital forcing is

Box 4.3**Airborne Fraction of a CO₂ Slug over Geologic Time****Equilibrium with the Ocean**

After a few centuries, a slug of new CO₂ added to the atmosphere will divide itself between the atmosphere and the ocean, with the ocean taking most but not all of the new carbon. The partitioning of the carbon between the air and the water will be determined by their relative sizes and the chemistry of the oceans. If there were no weathering and sedimentation reactions, the airborne fraction of the CO₂ at equilibrium with the ocean would remain at that level forever.

The airborne fraction at atmosphere-ocean equilibrium depends on the remaining strength of the carbonate buffer system chemistry (see box 3.1, “Carbonate System pH Chemistry”). For the relatively small amount of fossil fuel CO₂ already released, the buffer chemistry in the ocean will not be depleted too severely, and the airborne fraction at atmosphere-ocean equilibrium will be relatively low, about 15% in my model. As more carbon is released, the buffering effect gets weaker and the airborne fraction rises, up to 30% for a large, burning-all-the-coal scenario.

The solubility of CO₂ decreases as the temperature rises. Proxy measurements of the temperature of the deep ocean show that the deep ocean temperature got colder during glacial times and warmer during times of warm climate. Based on simple solubility, warming the ocean as expected would increase the airborne fraction of CO₂ slug by about 25%. A cautionary note is that these model results do not include the positive carbon cycle feedback that drove the atmospheric CO₂ variations through the glacial cycles, because the mechanism for that feedback is not understood.

Neutralization by the CaCO_3 pH-stat

The atmosphere-ocean equilibrium airborne fraction persists for a few millennia, until the ocean pH-stat in the CaCO_3 cycle replenishes the buffer capacity of the ocean. The ocean is neutralized by excess CaCO_3 dissolution over sedimentation, and the excess CaCO_3 can come from the land surface or the seafloor. There is essentially an unlimited amount of CaCO_3 available to dissolve on land, enough to neutralize a fossil fuel CO_2 slug no matter how large. Dissolution of CaCO_3 on the seafloor proceeds until the carbonates get covered with a layer of non-reactive clays, like the clay layer in sediments from the Paleocene-Eocene Thermal Maximum event (PETM; see chapter 2). There is thought to be enough available CaCO_3 on the seafloor to neutralize several thousand Gton C of fossil fuel carbon, a sizable burn.

Maybe 10,000 years from now the carbon cycle will have settled into another stable steady state, where the fluxes of CaCO_3 into and out of the ocean are in balance. As the pH and the buffer chemistry of the ocean recover, the capacity of the ocean to absorb CO_2 recovers as well, pulling the airborne fraction of a CO_2 release down to perhaps 10% of the total CO_2 slug released. After the carbon cycle reaches atmosphere-ocean- CaCO_3 equilibrium, the final processing of the fossil fuel CO_2 is left to the weathering CO_2 thermostat.

The Weathering CO_2 Thermostat

Ultimately the carbon makes it way back to the solid Earth by reaction with the CaO component of igneous rocks, producing sedimentary CaCO_3 . The time constant for this climate-stabilizing mechanism is hundreds of thousands of years, based on model calculations and from the timing of the PETM

(Box 4.3 continued)

(see chapter 2). The temperature record from the PETM, reconstructed from oxygen isotopes, looks like a sudden sawtooth in the midst of a fairly stable hothouse climate system. The future may be more complicated, since the climate impact of the long tail of the new CO₂ will interact with the ongoing instability of the glacial/interglacial cycles (see chapter 4).

Further reading: Archer 2005.

presumably the ultimate trigger, and the carbon cycle amplifies this Northern Hemisphere forcing into a global response.

Now, on a time scale of decades, the carbon cycle is absorbing the blow of the global warming climate event by taking CO₂ out of the atmosphere, a stabilizing negative feedback. Does this mean that the carbon cycle will eventually switch roles on us in the future, amplifying global warming?

There are other differences between the glacial cycles and global warming than timing. The glacial cycles were instigated by changes in temperature, resulting from the distribution of sunlight in latitude and season and amplified by the albedo change from the ice sheets. Some positive carbon cycle feedback drove atmospheric CO₂ to further amplify the temperature swings.

Today, the Earth's system is being driven by changes to CO₂ directly. The carbon cycle is inhaling because it is driven by the higher concentration of CO₂ in the atmosphere. Eventually, however, climate warming might drive the carbon cycle to begin exhaling.

Future Carbon Cycle Feedbacks

It's not easy to predict how the land biosphere carbon reservoir will play its hand, whether it will dump carbon or hoard it in response to human CO₂ emission. The problem is that it's not clear what processes or mechanisms are controlling the carbon uptake of the land surface today, making it difficult to project into the future. Also, humankind controls a lot of the land surface, so predicting its behavior as a carbon reservoir in the coming century is as much a sociological question as a physical science one.

But there are powerful reasons to worry that the land biosphere could release more than it takes up with an intensification of warming. The concentration of organic carbon in soils is a strong function of temperature. This is because when a leaf falls into the dirt, it decomposes more quickly in warm conditions than colder ones (see box 1.4, "Photosynthesis and Respiration"). Generally, the rates of biological processes such as decomposition more-or-less double in response to 10°C of warming (up to a point, until the biomolecular machinery starts breaking down). Soil carbon levels are highest in the chilly high latitudes and very low in tropical soils, even in rain forests that are lush aboveground, because the carbon decomposes more quickly in the tropical soils.

Soil carbon concentrations could change dramatically in high latitudes where peat deposits are currently preserved from degradation by being frozen in soils called permafrosts. Peats are thought to contain hundreds of

Gton C. Permafrost soils, depending on their thickness, can take centuries to melt, and have been melting back naturally for centuries since the end of the Little Ice Age, around the year 1830 (Lemke et al. 2007).

There is a zone near the soil surface, called the “active zone,” that melts in summer and refreezes in winter. This seasonally melted zone has been getting thicker over the past few decades in response to climate warming, potentially exposing more carbon in soils to degradation. Lakes also provide a pathway for degrading permafrost carbon around their boundaries, where the liquid water encounters the frozen soil. The anoxic condition of lake sediments provokes anaerobic fermentation of the carbon, producing methane as well as CO_2 , which reach the atmosphere in rings of bubbles around the lake periphery (Walter et al. 2006).

Another carbon reservoir to watch out for is the methane hydrates in the ocean. These are described more completely in chapter 5, but it is worth noting for now that a warming of the sediment column could provoke these ices to melt, potentially releasing their methane into the ocean or the atmosphere. The potential of methane hydrates to alter the future climate is huge, but it will take millennia for global warming to penetrate the sediment column where most of the hydrate is. Methane hydrates therefore would probably add to the global warming climate event only in the very long term (Archer 2007).

In the end, there is more carbon available as fossil fuel than the land surface could possibly take up or give off, so in a business-as-usual scenario the carbon fluxes

from the land surface would probably be smaller than the human fluxes. Hydrates in the ocean could potentially release as much carbon as humans do, probably over thousands of years. The fossil fuel carbon will be joined by whatever feedback carbon shows up, to share a common fate of dissolution into the ocean and slow reabsorption into the Earth by the CaCO_3 pH-stat and the weathering CO_2 thermostat.

The Fate of Fossil Fuel CO_2 in the Carbon Cycle

Although 70% of the Earth's surface is covered by ocean, most of the volume of the ocean, the cold abyssal water, is in contact with the atmosphere only in the coldest of places and times: the high latitudes in winter. In these places there may be sea ice separating air from water and slowing the CO_2 invasion of the deep sea even further. This bottleneck of getting gases into the abyss is why CO_2 uptake in the deep ocean takes much longer than one would expect based on the kinetics of gas exchange alone (see box 4.2, "Air-Sea Exchange of CO_2 Gas").

The overturning circulation of the ocean, which carries surface waters laden with fossil fuel CO_2 into the deep, could decrease with climate change, slowing CO_2 uptake into the deep ocean. This circulation is driven by the production of very dense waters in high latitudes, but temperatures in high latitudes will rise and, more important, rainfall will increase, leaving surface waters fresher, warmer, and therefore less dense than they used to be. The result could be a period of stagnation, lasting

Box 4.4**The Carbon Cycle Orrery**

This box is just for fun. The serious reader with lots of important serious things to do should feel free to skip it, with my blessing.

An orrery is a model of the solar system used by early astronomers to forecast the movements of the planets. The models were built before Kepler figured out that planets move in ellipses, so the trajectories of the model planets were composed of circles superimposed on other circles—"epicycles," they called them. An orrery doesn't represent the underlying mechanics of the real situation, but it comes up with a similar answer, although for the wrong reasons. Playing with an imaginary carbon cycle orrery is a useful way to understand the some of the moves of the real carbon cycle.

An antique orrery, precision handcrafted of solder and brass, carries with it some of the culture of Victorian-era science. This culture can also be tasted in samples of the language from early scientific papers on climate change.

Here I give practical effect to a desire which I had previously entertained,¹ to construct an orrery representation of the carbon cycle. I should certainly not have undertaken these tedious endeavors if an extraordinary interest had not been connected with them.² At an early stage of the investigation, I experienced the need of a first-class³ plumbing system. A great many factors which influence the carbon cycle in nature . . . [and] determine the quantitative relation between the natural movements of this gas and the amounts produced by the combustion of fossil fuel⁴ may find their equivalent here within the draining fluids, which may carry some insight into the enterprise of the carbon cycle. Although it is not possible to obtain exact quantitative expressions for the reactions in nature by which carbonic acid

[CO₂] is developed or consumed, nevertheless there are some factors, of which one may get an approximately true estimate [from the carbon cycle orrery], and from which certain conclusions that throw light on the question may be drawn.⁵

At the heart of the orrery is a lever, suspended on a swivel in the middle like a seesaw (figure 10). Call this the “pH balance.” Vertical glass columns capable of holding water are

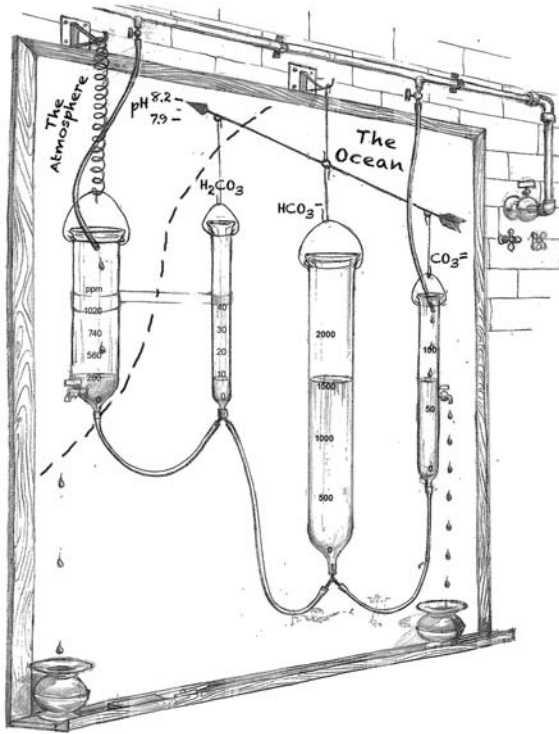


Figure 10. Artist's conception of the carbon cycle orrery.
(Illustration by Jill Wright)

(Box 4.4 continued)

suspended from the pH balance, with the water levels in the columns representing the concentrations of the carbonate buffer system chemistry of the ocean. The water level in the column on the left-hand side represents acid forms of carbon: dissolved CO_2 and carbonic acid (H_2CO_3), collectively called H_2CO_3^* (see box 3.1, “Carbonate System Equilibrium Chemistry”). The neutral carbon form is bicarbonate ion (HCO_3^-), and is represented in the middle, and the basic form, carbonate ion ($\text{CO}_3^{=}$), is represented by the right-hand arm. The columns are connected to each other by capillary tubing, permitting the water to seek a common water level in all three columns.

Attached to the CO_2 column is a parallel column representing atmospheric pCO_2 . Here we find the CO_2 thermostat. Water flows into the atmospheric CO_2 column at a rate determined by the setting of a valve. This is analogous to CO_2 outgassing from the Earth. Water flows out of the column through a trickle drain at the base of the column, analogous to the weathering that puts carbon back into the solid Earth as sedimentary CaCO_3 . At some water column height, there is enough pressure in the cylinder to push water out the drain as fast as it comes in from above. The CO_2 -stat column adjusts its water level in order to balance its flows. The atmospheric CO_2 column needs to remain on the same vertical level as the ocean H_2CO_3^* column, because Henry's law relates pCO_2 and H_2CO_3^* , regardless of the concentrations of HCO_3^- and $\text{CO}_3^{=}$. These columns are therefore attached to each other and ride up and down together.

The carbonate ion ($\text{CO}_3^{=}$) column also has water trickling through it, representing the CaCO_3 cycle pH-stat. Water flows in the top, representing weathering input of dissolved ingredients for CaCO_3 , and flows out a trickle drain located partway up the column, representing burial of CaCO_3 in ocean sediments. The height of the drain on the column represents the

saturation $\text{CO}_3^{=}$ concentration in equilibrium with CaCO_3 . The water level eventually reaches an equilibrium where the flow out equals the flow in. This column is gaining and losing water ten or twenty times faster than the atmospheric CO_2 column does, so that the pH-stat column will reach equilibrium ten or twenty times faster than the CO_2 -stat column will.

Perhaps it will be easiest if we observe the orrery in action, simulating the response of the carbon cycle to the release of a slug of new carbon as CO_2 to the atmosphere. At the outset, the orrery is in equilibrium. The water levels in the ocean chemistry tubes are all equalized, the atmospheric CO_2 is equalized with ocean dissolved CO_2 , and the inflow and outflow rates of the atmospheric CO_2 and ocean CO_3 columns are balanced, with outflow equaling inflow. This state is diagrammed in figure 11a.

The CO_2 release is simulated by pouring a cup of water into the atmospheric CO_2 column. The atmospheric CO_2 column drains into the ocean CO_2 column, their equalizing water levels representing the equilibration of CO_2 between the atmosphere and the ocean.

Putting more water on the H_2CO_3^* side of the pH balance tips the scales, lowering the H_2CO_3^* column and raising the $\text{CO}_3^{=}$ column (figure 11b). The pointer on the left-hand side of the pH balance indicates that the ocean has been acidified.

Next, the water levels equilibrate between the ocean chemistry columns. The water level in the CO_2 side has been elevated by the newly added water, and the $\text{CO}_3^{=}$ side has been elevated by the tipping pH balance. So water flows from both the outside columns into the center column, representing the chemical reaction



until it reaches equilibrium, represented in the orrery as equalized water levels between the three columns.

(Box 4.4 continued)

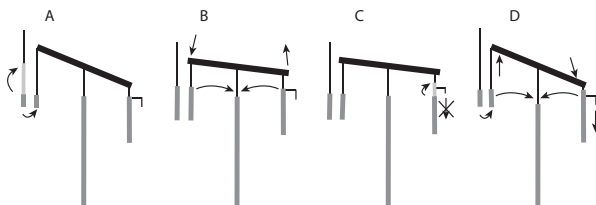


Figure 11. Schematic functioning of the carbon cycle orrery.

The changes in water levels have perturbed the two drip-through feedback systems, the CO_2 thermostat on the atmospheric CO_2 column, and the pH-stat on the $\text{CO}_3^{=}$ column. On the CO_2 side the water level is higher than equilibrium, because of the newly added water, and the feedback drains it down. Ocean $\text{CO}_3^{=}$ is now lower than equilibrium, depleted by reaction with CO_2 , and the feedback pushes it back up (figure 11c).

The pH-stat on the ocean $\text{CO}_3^{=}$ column finds its equilibrium more quickly than the CO_2 -stat because its through-flow is faster. As the through-flow replenishes the water in the $\text{CO}_3^{=}$ column, it tips the pH balance back toward its original position, neutralizing the acid of the added CO_2 (figure 11d). The swivel plus the added water to the $\text{CO}_3^{=}$ column causes water to flow from both the CO_2 and the $\text{CO}_3^{=}$ columns into the HCO_3^{-} column, a continuation of the chemical reaction (1).

As the pH balance tips up toward higher pH, it lifts the H_2CO_3^* column, and water drains out into the ocean HCO_3^{-} column. When the water level falls in the H_2CO_3^* column, it also falls in the atmospheric CO_2 column. The orrery demonstrates how the CaCO_3 pH-stat restores the pH of the ocean and allows the ocean to take out a bit more CO_2 from the atmosphere.

The CO_2 stat adjusts the atmospheric CO_2 concentration so slowly that it is not far wrong to imagine it decreasing the

water levels in all three of the ocean carbon chemistry columns, filling up and draining down of the entire CO_2 reservoir of the ocean, without altering the pH all that much.

The orrery could produce a high- CO_2 hothouse world by increasing the trickle flow rate of water into the atmospheric CO_2 column or impeding the outflow. Atmospheric CO_2 would slowly rise, increasing the water level in the ocean H_2CO_3^* column. The water level in the ocean $\text{CO}_3^{=}$ column would be continuously stabilized by the pH-stat drip-through system because the rise in atmospheric CO_2 is gradual enough that the pH-stat can keep up, in contrast to the fossil fuel emission scenario. In the end, the atmospheric CO_2 stat controls the water levels in all the columns, but the CaCO_3 pH-stat gets to insist on an appropriate $\text{CO}_3^{=}$ concentration in the ocean by setting its pH.

The orrery must be carefully tuned to work right, and there are ways it could be tuned that would not be possible in the real world. For example, if the capillary tubes connecting the ocean chemistry columns were too large, water would flow between the columns faster than the swing response time of the pH balance. New water added to the CO_2 column would spread out to the other columns, the rising tide floating all boats, without affecting the pH balance at all. Real carbon chemistry can't work that way. The reason for the breakdown is that the underlying mechanisms controlling the orrery are not the same as those of the real carbon cycle. There may be value in imagining how the orrery works if it is tuned correctly, but it's probably not very useful to imagine alternative realities with it.

If we pass the above-mentioned processes for consuming and producing carbonic acid $[\text{CO}_2]$ under review, we find that they evidently do not stand in such a relation to or dependence on one another that any probability exists for the permanence of an equilibrium of the carbonic acid $[\text{CO}_2]$ in the atmosphere.

(Box 4.4 continued)

An increase or decrease of the supply continued during geological periods must, although it may not be important, conduce to remarkable alterations of the quantity of carbonic acid [CO₂] in the air, and there is no conceivable hindrance to imagining that this might in a certain geological period have been several times greater, or on the other hand considerably less, than now.⁶

NOTES

1. John Tyndall, On the absorption and radiation of heat by gases and vapours, and on the physical connexion of radiation, absorption, and conduction, *Philosophical Magazine*, ser. 4, no. 22 (1861): 169–94, 169.
2. Svante Arrhenius, On the influence of carbonic acid in the air upon the temperature of the ground, *London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, ser. 5, vol. 41, no. 251 (1896): 237–76, 267.
3. Tyndall 1861, 170.
4. G. S. Callendar, The artificial production of carbon dioxide and its influence on climate, *Quarterly Journal of the Royal Meteorological Society* 64 (1938): 223–40, 224.
5. Prof. Hogbom, transl. Arrhenius 1896, 269.
6. *Ibid.*, 273.

centuries or longer, that could impede the invasion of CO₂ into the deep ocean.

The accelerating rise of atmospheric CO₂ tends to drive CO₂ invasion into the ocean more quickly. Counteracting this is depletion of the buffer chemistry of surface seawater. In general, doubling the CO₂ halves the CO₃⁼ concentration in seawater, halving the ability of

the seawater to absorb more CO_2 (see box 3.1, “Carbonate System pH Chemistry”). The higher atmospheric CO_2 goes, the weaker the ocean buffer will become.

And then there is the question of the glacial CO_2 cycles. This was a positive feedback, originating in the oceans and releasing CO_2 when temperatures rose, as explained in chapter 3. Our ignorance of how this happened undermines our confidence in predicting the future. If the unidentified positive feedback from the past rears its head in the future, it would make the CO_2 airborne fraction higher than what the models predict.

After the slug of new CO_2 spreads out and equilibrates between the atmosphere and the ocean, the $p\text{CO}_2$ of the atmosphere remains higher than it would have been for what carbon cycle modelers call the long tail. The residual airborne fraction of the CO_2 slug awaits neutralization by the CaCO_3 pH-stat and ultimate burial by the weathering CO_2 thermostat (see box 4.3, “Airborne Fraction of a CO_2 Slug over Geologic Time”).

The time constant for the weathering CO_2 thermostat (see chapter 2) is hundreds of thousands of years, similar to the oscillation time of the glacial/interglacial cycles. This means that the future evolution of climate on these time scales will probably be determined by the interaction of the CO_2 tail with the wobbles in Earth’s orbit around the sun.

In the natural course of events, a new Laurentide ice sheet in Canada will nucleate and begin growing at some point in the future. The glacial/interglacial cycles have taken 100,000 years overall, but the interglacial intervals

have been short, only about 10,000 years, and this is how long our current interglacial interval has already lasted (Hays, Imbrie, and Shackleton 1976). It initially seemed that the next ice age might be geologically imminent, that is to say it might start in just a few thousand years. (Note that in this context, the word “soon” has a different meaning for geologists than it usually does for, say, economists.)

However, the orbit of the Earth around the sun today is nearly circular, a state Earth revisits about every 400,000 years (Paillard 2001). All the points of the circle are the same distance from the sun, so this configuration eliminates much of the variation in sunlight intensity that drives the glacial cycles. The last time of circular orbit was 400,000 years ago, a time with a long interglacial interval that lasted 50,000 years. The past few glacial cycles have been driven by more intense orbital forcing than the next few glacial cycles will be. So it is entirely possible that the natural future evolution of Earth’s climate would be continued warmth for the next, say, 50,000 years, followed by gradual cooling driven by the growth of ice sheets in the northern high latitudes and a mysterious drawdown in atmospheric CO₂ concentration.

The effect of the long tail of fossil fuel CO₂ in the atmosphere will be to make it harder for ice sheets to nucleate and begin to grow in the Northern Hemisphere. The fossil fuel era may stave off the next ice age, which was due in 50,000 years but may now be delayed for 500,000 years (Archer and Ganapolski 2005).

The bottom line is that atmospheric CO₂ concentration will peak for a few centuries and then subside into

Box 4.5**How Much Carbon Is Too Much?**

Target concentrations of CO₂ in the air, discussed as limits not to be exceeded, have been dropping over the years. In the 1990s everyone talked about doubling the natural concentration, reaching about 560, as a target. But since then climate changes have become more concrete, in the form of droughts and melting ice, and if anything they are on the severe end of the forecasts. The targets scientists have been discussing have been ratcheting down, to 450 ppm and most recently to 350 ppm.

In the 1990s the Intergovernmental Panel on Climate Change created a set of hypothetical atmospheric CO₂ “stabilization scenarios,” trajectories in pCO₂ that wound up at various concentrations; 350, 450, 550, and 750 ppm were some commonly used values (Nakicenovic et al. 2000). Carbon cycle modelers were invited to use their models to determine how much CO₂ would have to be emitted in order to follow each trajectory. It turned out that there is a lot of wiggle room in the timing of emissions cuts to reach any given atmospheric CO₂ concentration, making it difficult to pin down exactly how quickly CO₂ emissions need to be cut.

One way to boil down the confusion is to think about the size of the entire slug of CO₂ ever emitted by humankind, rather than details of emissions now versus later. A few hundred years from now, when we look back and see how much warmer the Earth got, at its peak, from the human climate adventure, this is the factor that predicts it the best (Allen 2009; Meinshausen 2009).

A pCO₂ target of 450 ppm is based on a maximum temperature target of about 2°C, which would make the Earth warmer than it has been in millions of years. Two degrees is not an estimate of safety, exactly, but rather a turning point in the damage curve. Beyond 2°C the climate monsters, as Steve Pacala calls

(Box 4.5 continued)

them, start getting a new kind of scary. Earth's climate could reach this level in response to a CO₂ slug of about 700 Gton C. After peaking at about 450 ppm, the atmospheric CO₂ concentration would plateau at about 350 ppm in the long tail.

A total CO₂ slug of about 700 Gton C turns out to be about the maximum that would avoid exceeding global warming of 2°C. 700 Gton C would result in an atmospheric CO₂ concentration of about 450 ppm at the peak, decaying to about 350 ppm in the long tail. Between fossil fuel combustion and deforestation, humankind is more than halfway to a limit of 700 Gton C.

The CO₂ slug worldview simplifies the regulatory picture for CO₂ emission regulation, because it says emit now, and you can't emit later. Slow down gradually now, or more abruptly later. Some hypothetical rates of CO₂ emission are plotted in figure 12. The solid line is business as usual, with an annual rate of increase of 1.4% per year. The dashed-line scenarios each begin at different times, in the years 2010, 2020, 2030, and 2040. The rate of scaling back the carbon emissions for each scenario was adjusted to keep the total CO₂ slug at 700 Gton C for all scenarios.

If we begin to cut back in the year 2010, cuts of 2% per year would be required to come in on budget (figure 12, bottom plot). Beginning in 2020, we'd need 3.5% per year cuts. Beginning in 2030, we'd need cuts of 7% per year, and by 2040 we'd need cuts of 35% per year. Replacing energy infrastructure costs money, and the faster we have to do it, the more it will cost.

An atmospheric CO₂ concentration of 350 ppm may actually be a reasonable marker for honest safety. It is based on a concept called committed warming, which is warming in the pipeline from the CO₂ already released. The argument is that dangerous stuff is already happening, in droughts and extreme weather events, and further warming is clearly dangerous. The

THE PRESENT AND FUTURE CARBON CYCLE

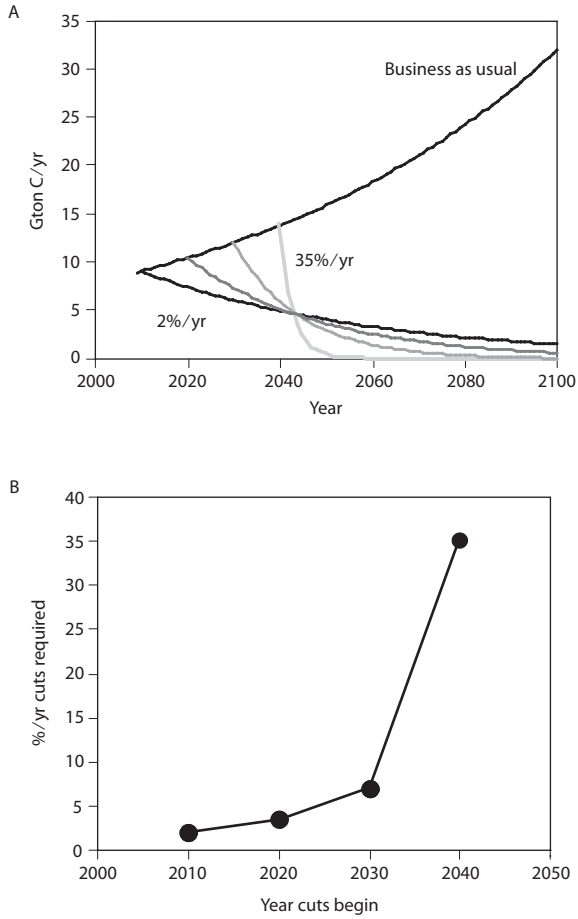


Figure 12. (a) CO₂ emissions pathways that would wind up with 700 Gton C in total. (b) Rate of emissions cuts that would be required, as a function of the year the cuts begin.

(Box 4.5 continued)

current concentration in the air is about 385 ppm, and if it were to decline to 350, the committed warming would be canceled and Earth would stop warming (Hansen 2006).

We are already over the line, but if CO₂ emission stopped suddenly, natural carbon sinks would draw the concentration down to 350 in a few decades. Acknowledging the reality that humankind is not going to go cold turkey on CO₂ emissions, ultimately reaching 350 may require active industrial removal of CO₂ from the atmosphere.

the long tail (see box 4.3, “Airborne Fraction of a CO₂ Slug over Geologic Time”). The long tail of global warming will have particular impact on slowly changing components of the climate system such as the ice sheets and permafrost soils. The full response of the sea level to changes in Earth’s temperature in the past was 100 times greater than the forecast for sea-level change in the year 2100 because it takes time to melt an ice sheet. We will also be entering the time realm of the spiteful saboteur wing of the carbon cycle. The long tail of global warming will be plenty long enough for ice sheets, permafrosts, and the carbon cycle to respond completely.

5 METHANE

Methane is like the radical wing of the carbon cycle in climate. This chapter summarizes the methane cycle and its potential for changes in the Anthropocene.

METHANE AND CLIMATE

The second most important human-released greenhouse gas, methane, is also a molecule based on carbon. CO_2 accounts for about half of the warming forcing overall, while methane accounts for about a quarter (Forster et al. 2007). The remaining radiative forcing arises mostly from nitrogen dioxide (N_2O) and hydrocarbons such as freons. The concentration of methane is about double what it was in the year 1750, a larger relative increase than for CO_2 . But the rise in atmospheric methane with time has been erratic, making it difficult to predict the future.

Molecule per molecule, methane is about forty times more powerful than CO_2 as a greenhouse gas. The difference in radiative forcing per molecule between CO_2 and CH_4 arises because of the band saturation effect,

wherein the strongest absorption frequencies (bands) begin to absorb all of the IR light (saturate). There are fewer methane molecules in the air than CO_2 molecules, but each one drives a larger change in climate because the methane bands are less saturated than are those of CO_2 (see box 5.1, “Greenhouse Properties of CO_2 and Methane”).

Comparisons of the greenhouse forcing strength of CO_2 and methane are confusing, because some calculations report the greenhouse intensity per molecule (or equivalently ppm in the atmosphere) while others, such as the Intergovernmental Panel on Climate Change, compare the impact per mass (which is less per methane than per CO_2 because oxygen is heavier than hydrogen) and also integrated over some time interval, say 100 years, to generate what are called global warming potentials. The global warming potential of 1 kg of methane is 21 times higher than for 1 kg of CO_2 .

Also, the radiative impact of a gas per molecule depends on its concentration, because of the band saturation effect. When you calculate the change in energy balance per change in concentration, the answer depends on exactly what concentration change you use to do the calculation, and from what initial concentration. The factor of 40 quoted here is based on the total change relative to the pre-anthropogenic era: 0.8 ppm driving a radiative forcing of 0.5 W/m^2 for methane, and 100 ppm driving a radiative forcing of 1.6 W/m^2 for CO_2 . If we were to ask what the effect of the next ppm change in concentration would be, or the next ppb change, we would get

a higher multiplier for methane, numbers like 60. Also, the methane cycle affects other greenhouse gases, such as water vapor, in the upper atmosphere, adding a bit to the radiative forcing of the methane. Suffice it to say that a little extra methane in the air goes a long way toward changing the climate.

Once methane carbon is oxidized to CO_2 , it accumulates just as if the CO_2 came from any other anthropogenic source. The CO_2 will equilibrate between the atmosphere and the ocean, leaving 15–35% in the air, regardless of whether the methane is oxidized in the atmosphere (in which case the airborne fraction would drop to equilibrium) or in the ocean (in which case it would rise to equilibrium). Thus the methane cycle has the potential to warm the Earth during the time period when it is released, and further to contribute to the accumulated burden of extra CO_2 in the long tail.

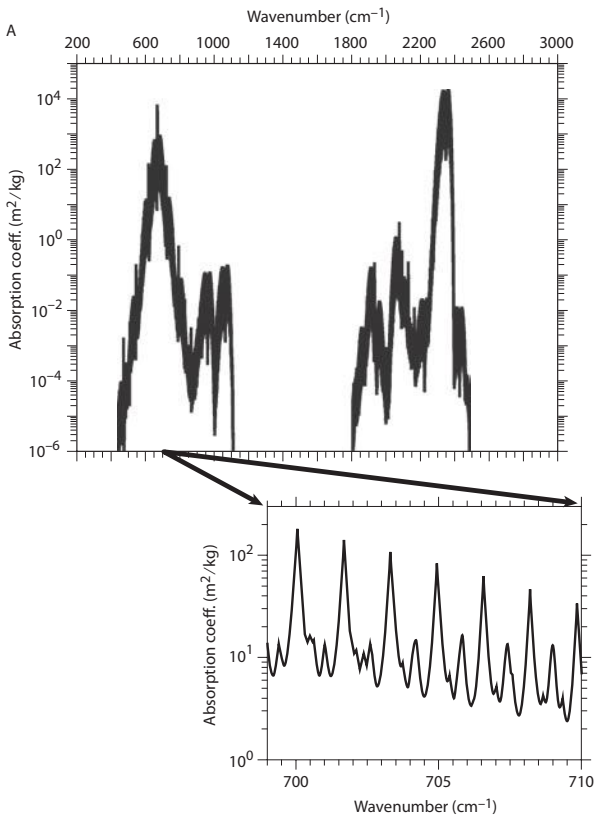
CONTROL OF ATMOSPHERIC METHANE CONCENTRATION

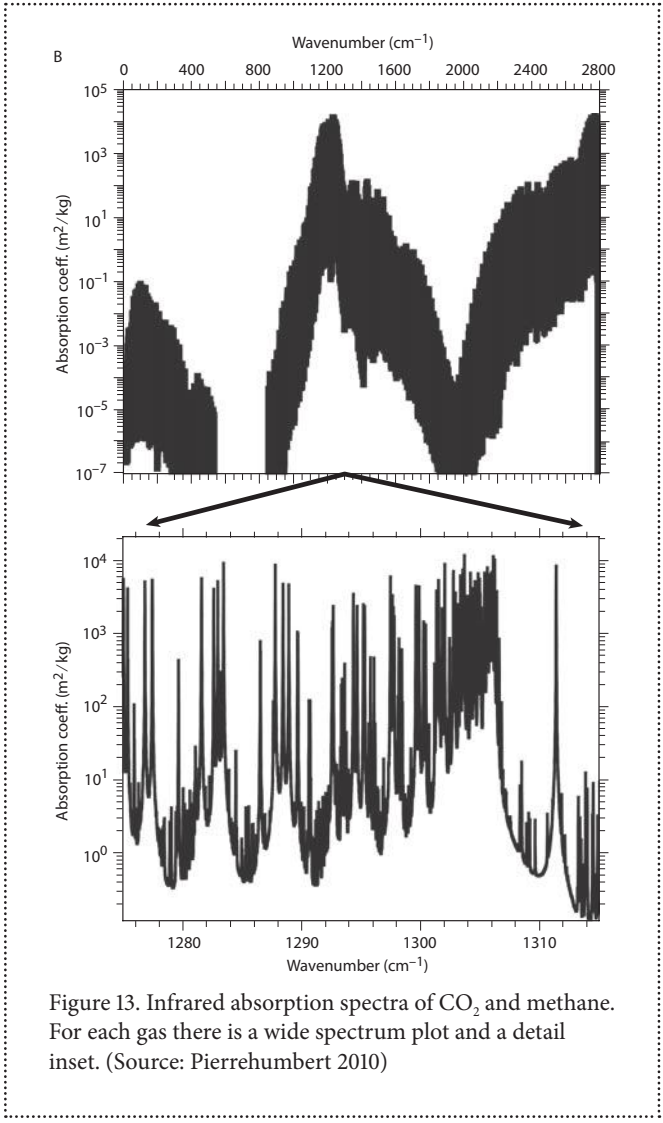
The concentration of methane in the atmosphere reacts very differently to human emission than CO_2 , because methane is a transient gas while CO_2 essentially accumulates in the atmosphere-ocean-land carbon cycle system. The concentration of methane in the air is determined by the balance between its sources and sinks, mostly by chemical reaction in the atmosphere. The lifetime of a molecule of methane in the atmosphere is about decade. Increase the rate of methane production (the source

Box 5.1

Greenhouse Properties of CO₂ and Methane

The infrared spectra of CO₂ and methane are shown in figure 13. The plots show how transparent or absorbing the gas is, expressed as the absorption coefficient on the vertical axis.





(Box 5.1 continued)

The scale is logarithmic, to compress a huge range into single plots spanning 10 orders of magnitude. The horizontal axis is the “color” of the light, expressed as the number of waves per centimeter, called the wave number, in units of cm^{-1} .

The spectra are immensely complicated and spikey, meaning that some frequencies of light absorb very strongly while others, nearby in the spectrum, absorb much less. The spikes are so numerous that in the plots of the spectra over a wide range of frequencies, they all run together on the plot, and it just looks like fuzz. But in the zoomed-in sections, detailed structure can be seen.

The frequencies are determined by the vibrational modes of each molecule, each of which has a fundamental frequency and harmonics like the ringing of a gong. The frequencies may also be affected by rotation of the molecules, although this is more important for polar molecules like water vapor.

A greenhouse gas is able to absorb infrared radiation (IR) coming up from the ground, and it also emits IR at the same frequencies. Because the gases in the upper part of the troposphere are colder than the ground temperature, the IR emitted from the gas will be at lower intensity than the IR from the ground. The net effect, viewed from space, is a replacement of the warm IR from the ground with cold IR from the upper troposphere (figure 14).

The absorption band for CO_2 that matters most for climate is the one near 700 cm^{-1} , because this coincides with the peak of the IR light coming from the ground. This band comes from the bending vibrational mode of CO_2 . For methane, the absorption band near $1,300 \text{ cm}^{-1}$ is the most climatically significant.

A change in total IR intensity from adding a greenhouse gas, in units of Watts/m^2 , is called the radiative forcing of the

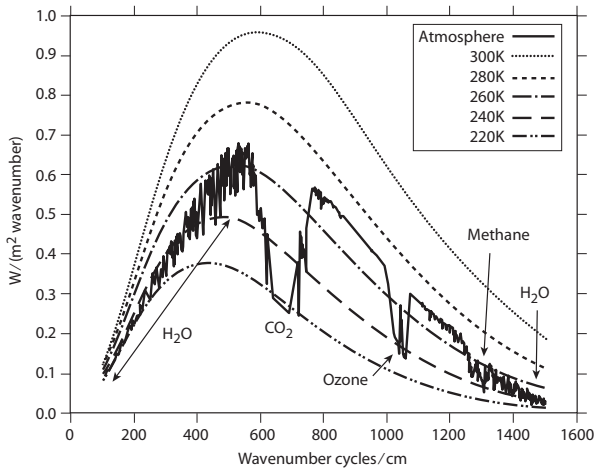


Figure 14. Outgoing infrared radiation from the Earth as predicted by a model. (Source: Archer 2006)

gas. A plot of radiative forcings calculated for CO_2 and CH_4 as a function of concentration is given in figure 15.

The spikiness of the absorption spectra leads to a phenomenon known as the band saturation effect. When a greenhouse gas is very dilute, only the tallest spikes in the spectrum absorb much light. With more gas, the light corresponding to the tallest spikes is completely absorbed. The absorption of this particular frequency no longer cares how much gas is there, because the light is all gone. But the next-tier spikes have begun to absorb light.

The result is that the amount of IR light absorbed over all frequencies is very sensitive to the concentration when the concentration is low, because the absorption bands are unsaturated and adding more gas absorbs lots more light. As

(Box 5.1 continued)

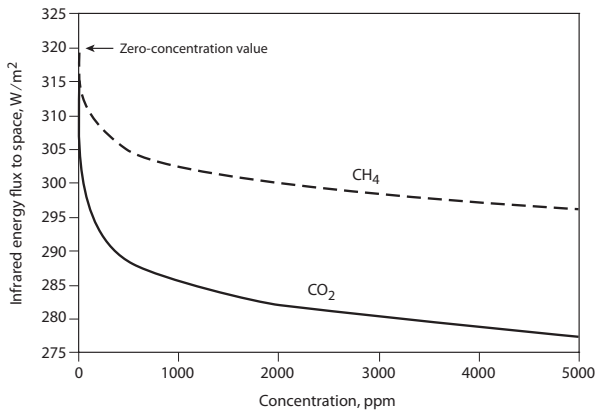


Figure 15. Outgoing infrared energy flux through a column of tropical atmosphere as a function of the concentrations of CO₂ and methane.

the concentration increases, the radiative forcing curve flattens out, becoming less sensitive to the concentration.

For CO₂, the radiative forcing follows very closely a simple logarithmic function of concentration. Perhaps this is because the CO₂ absorption peak (see figure 15) near 700 cm⁻¹, the climatically important one, is nearly perfectly cone-shaped when plotted in log linear space.

Because of the logarithmic curve, the radiative forcing is proportional to the number of “doublings” of atmospheric CO₂ concentration, which can be calculated as

$$\text{Radiative forcing [W/m}^2\text{]} = -3.5 \text{ W/m}^2 \ln(\text{pCO}_2/280)/\ln(2).$$

Since the equilibrium temperature of the Earth scales linearly with the radiative forcing, it is also linearly dependent on the number of CO₂ concentration doublings:

$$\Delta T = \Delta T_{2x} \ln(p\text{CO}_2/280)/\ln(2),$$

where ΔT_{2x} is the climate sensitivity (see box 2.4, “The Climate Sensitivity Parameter”).

For methane, the effect of its concentration on its radiative forcing is broadly similar to that of CO_2 , in that band saturation decreases the sensitivity at higher concentrations. For a given concentration, the radiative forcing from CO_2 is greater because CO_2 absorbs in the peak of the terrestrial infrared radiation, while methane is more on the fringe. The methane curve is not as close to a simple log function as the CO_2 curve is.

flux), and the concentration in the atmosphere would rise for a decade or two until a new steady state concentration is reached (see box 5.2, “The Kinetics of a Transient Gas in the Atmosphere”).

CHANGES IN METHANE PRODUCTION

There are many natural sources of methane to the atmosphere, which we have supplemented by sources of our own such as rice farming and ruminant animal husbandry (Denman 1973).

Most, nearly all, of the methane in the atmosphere owes its origin ultimately to photosynthesis of organic carbon. It is possible that some reducing power comes up from the interior of the Earth, in the form of methane, or as hydrogen that reacts with CO_2 to form methane, but this is negligible compared with production of reduced carbon from photosynthesis. The prebiotic

Box 5.2**The Kinetics of a Transient Gas in the Atmosphere**

The life cycles of many gases in the atmosphere follow simple rate equations that are analogous to radioactive decay. The rate of gas loss depends on the amount of gas present, just as the number of counts on a Geiger counter will depend on the amount of radioactive stuff there is present. The astute reader may have surmised from chapters 1 through 4 that CO_2 is more complicated than this, with multiple stages in the recovery of the carbon cycle to addition of a slug of new CO_2 .

But many trace gases are simpler, methane included. The concentration of such a gas changes with time when the rate of its production is not equal to the rate of decomposition. If we take the decomposition rate to be equal to a constant, k , times the concentration, C , we get

$$dC/dt = P - k C, \quad (1)$$

where dC/dt is the rate of change of concentration of the gas per time. If C is low, dC/dt is positive, and the concentration C will grow. If C is too large, dC/dt is negative, and C falls.

There is an equilibrium in this system, which the concentration will reach if the production rate P and the degradation rate constant k remain constant for long enough. By assuming dC/dt is zero, the steady state inventory can be calculated to be

$$C = P/k.$$

This shows that the steady-state concentration (C) of a gas like methane will go up if it is produced faster (increase in P) or if it lives longer (decrease in the rate constant for degradation, k). The concentration will approach equilibrium on a time scale determined by the rate constant, k .

The response of atmospheric methane concentration to the emission rate depends on the time scale of the emission relative to the life time of the gas. If methane is released all at once (catastrophically), you get a spike that subsides. If it is released over hundreds of years (chronically), you get an increase in the steady-state concentration.

theory of petroleum is one of those ideas that will never die.

The organic carbon can react to yield methane either biologically, mediated by the microorganisms called archaea, or abiotically, by cooking the carbon deep in the Earth. Most of the methane in the atmosphere comes from the former, “biogenic” sources rather than from the “thermogenic” sources. The microorganisms that produce methane, the archaea, are obligate anaerobes; the molecular oxygen in our atmosphere is poison to them. Therefore, biogenic methanogenesis takes place only in special, limited settings.

Wetlands

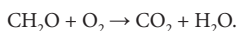
The main such setting is in swamps and bogs. When organic carbon is covered with water, it gets cut off from the oxygen in the air. The methane flux from soils is extremely sensitive to changes in the water table, releasing CO₂ when it dries and bubbling up swamp gas, methane, when it gets flooded.

Natural wetlands come and go, leaving an ice core record of very fast changes in atmospheric methane

Box 5.3**Methanogenesis Chemistry**

Methane is the most reduced form of carbon. It is not produced directly by photosynthesis because it has no real use in the biochemical machinery. A very reduced form of carbon is useful for long-term energy storage, but methane gas would leak away, as opposed to lipids, which store energy nearly as well and are easier to hang on to (see box 1.5, “Biochemistry 101”).

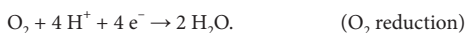
Methane is formed for the most part as a by-product of a respiration reaction. Respiration is the chemical reaction by which organic carbon is oxidized to yield its energy, the energy originally captured in photosynthesis. When we as multicellular organisms respire our lunch, we react the reduced carbon with molecular oxygen. The reaction is



This can be decomposed into two electrochemical “half-reactions,” in which the transfer of electrons is revealed:

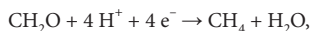


and

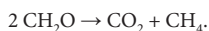


The organic carbon in the CH_2O releases four electrons, e^- , when it becomes CO_2 on the right-hand side of the C oxidation reaction. Since free electrons do not run around much on their own in the ocean, the C oxidation reaction has to be accompanied by a complementary reaction that takes up the electrons. In this case, molecular oxygen, O_2 , takes up the electrons to make H_2O . Molecular oxygen is called the electron acceptor in the oxic respiration reaction.

Bacteria can use other electron acceptors if there is no oxygen. Examples include nitrate (NO_3^-) becoming nitrogen gas (N_2), sulfate (SO_4^{2-}) becoming sulfide (H_2S), and also, surprisingly, organic carbon itself (CH_2O), forming CO_2 and methane (CH_4). The half-reaction is

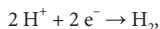


and the overall reaction

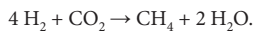


It is not intuitively obvious to me that one could get energy by taking two carbons in an intermediate oxidation state (CH_2O) and oxidizing one while reducing the other. This seems to me like taking two half-charged batteries and getting energy out by draining one battery into the other. At any rate, this conversion does seem to yield energy, and a by-product of that energy extraction is the production of methane.

There are many pathways for getting from organic carbon to methane; the reaction doesn't happen mechanically in such a simple way (Whiticar and Faber 1986). Most of the methane produced on Earth owes its existence to biology, and most of the so-called "biogenic" methane is produced from hydrogen gas, H_2 . Hydrogen gas is produced essentially by using hydrogen ions from water as an electron acceptor:



and reacting the hydrogen with CO_2 to produce methane:

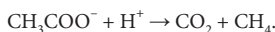


The overall gist of it remains the same, namely, that organic carbon provides the reducing power to produce methane.

Another major pathway for producing methane involves acetate (CH_3COO^-). Acetate is essentially a CO_2 molecule

(Box 5.3 continued)

fastened to a methane, and microorganisms, the archaea in particular, can make a living by splitting it in a fermentation reaction.



Acetate fermentation is the dominant pathway for methane production in freshwater settings, while CO_2 reduction by H_2 is the dominant pathway in marine settings.

concentration changes (see figure 4). The concentration of methane was lower in the glacial climate because of the general aridity. Methane played a similar role during thousand-year climate flip-flops called Dansgaard-Oeschger events, giving us an indication of the global impact of these North Atlantic-centered events. The methane cycle is amplifying the climate changes, just as the carbon cycle does, by removing greenhouse gases in response to cooling (variations in Earth's orbit driving changes in ice sheet albedo). However, the methane cycles are a weaker driver of climate than the CO_2 cycles are.

Artificial wetlands are mostly associated with rice cultivation. Rice was first cultivated 10,000 years ago, and humans probably eat more rice than anything else. Rice does not require swampy conditions to grow, but the grassy plants tolerate submergence better than weed species and animal grazers, so rice requires much less labor to grow in inundated soil. Rice farming is a significant artificial source of methane to the atmosphere (table 1).

Table 1
Methane Sources and Sinks

	<i>Tg CH₄/yr</i>	<i>Gton C/yr</i>
Natural sources		
Wetlands	200	0.150
Termites	20	0.015
Geological	10	0.008
Total natural sources	230	0.173
Artificial sources		
Rice farming	50	0.038
Ruminants	80	0.060
Energy industry	90	0.068
Landfills	50	0.038
Biomass burning	40	0.030
Total artificial sources	310	0.233
Total sources	540	0.405
Sinks		
Tropospheric OH	450	0.338
Soils	20	0.015
Stratosphere	40	0.030
Total sinks	510	0.383

Source: Denman et al. 2006.

Methane mostly comes from freshwater systems, because seawater contains high concentrations of sulfate (SO_4^{2-}) that serves as an electron acceptor, a different way to eat organic carbon after oxygen is gone but without making methane (see box 1.4, “Photosynthesis and Respiration”). Sulfate deposition in acid rain inhibits methane production in soils, and sulfate in the ocean inhibits methanogenesis in sediments, until you get deep enough in the sediment that the sulfate is all gone.

Anaerobic Digestion of Cellulose

Grazing animals and termites maintain anoxic environments for microbial digestion of cellulose. The microbes, mostly archaea, are necessary because multicellular animals, with the exception of some types of termites, have never evolved an enzyme to break up cellulose. Cellulose is built from ordinary sugar molecules, like starch (see box 1.5, “Biochemistry 101”), only the chemical bond between adjacent sugars in cellulose is twisted in a way that our enzymes can’t process, like an itch they can’t scratch. Cellulose is the most abundant large molecule in the biosphere. Usually, evolution figures out a way to take advantages of opportunities like this, so I find it surprising that the archaea have cornered the market for cellulose. Could it be a biochemical evolutionary evasive maneuver on the part of the plants? You decide.

Cows are an example of ruminant animals, which have an anoxic microbial incubator organ in the early parts of their stomachs. Horses are hindgut fermenters, providing an environment for the microbes in their large intestine. Humans and pigs have a rudimentary incubator called the colon. Termites do it in their guts. These organs sustain a complex consortium of interdependent microorganisms, bacteria and archaea, that together make up a sophisticated chemical reactor system. The archaea ferment cellulose into acetate, which they then split into CO_2 and methane.

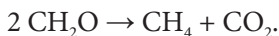
Making use of cellulose is a hurdle to biofuel production, too, where the goal is to produce ethanol, a liquid

fuel suitable for transportation. Splitting up the cellulose requires use of enzymes, generally extracts of the micro-organisms rather than maintaining the critters alive the way the termites and cows do it.

Methane in the Ocean

In spite of inhibition by seawater sulfate (SO_4^{2-}), there is a massive methane cycle in the ocean, in particular in sediments beneath the seafloor. The rates of methane production are definitely slower than in swamps. But the deep sediments have the advantage of a way to store huge amounts of methane, as frozen water- CH_4 structures known as methane hydrates.

Most of the methane produced in sediments comes from organic carbon through a reaction like



There are two main biochemical pathways, depending on the setting, freshwater or marine (see box 5.3, “Methanogenesis Chemistry”). In deep sediments, at higher temperature, simple heating of organic matter can also produce methane. The bottom line in any case is the same, with the reducing power coming from organic carbon. “Thermogenic” methane is marked by a different signature in carbon isotopes (about -30‰ instead of around -60‰ for biogenic). Thermogenic methane also has more longer-chain carbon molecules in it, potentially affecting the stability and optimal structure of the hydrates. The methane in the Gulf of Mexico, and

those of the West Siberian Plain, are thermogenic, but most other methane deposits are of biological origin (Milkov 2005).

Methane in the ocean can take the form of bubbles of gas, even at great pressures, and it dissolves in seawater to some extent. At high pressure and cool temperatures, methane and water can freeze together into an icy structure called clathrate or hydrate. Water molecules form a cage structure like a soccer ball, enclosing a molecule of some gas. There are no chemical bonds between the gas and the water molecules, so the size of the gas molecule is the only thing that matters. CO₂ hydrates probably form on Mars, in high latitudes under pressure of ice sheets. Most of the hydrates on Earth contain methane.

Hydrates require a pressure many times higher than the atmospheric pressure, and cool temperatures. Even if you have a bubble of pure methane at one atmosphere pressure, there is not enough methane dissolved in the water around the bubble to form hydrate. Nearshore sediments of the ocean are a good place to find hydrates, because the sediments tend to be carbon-rich, supplying methane, and because they have suitable pressure and temperature conditions. Throughout most of the world's ocean, hydrates can be found in sediments under about 500 meters of water or more. On land, hydrates are usually associated with deep gas deposits in high latitudes, particularly in the Arctic.

The hydrates in the ocean contain a massive amount of methane. Estimates vary by an order of magnitude,

but they are generally in the thousands of Gton C. There is more hydrate than the oil and traditional gas reserves in the fossil fuel industry, around 200 Gton C each, and maybe even as much as the coal, about 5,000 Gton C (Archer 2007).

Hydrates in the climate system seem intrinsically frightening. Methane hydrate is physically unstable anywhere on the surface of Earth, because the pressure is too low. Any hydrate that you put in such unfavorable conditions will melt, or recrystallize to water ice, releasing its methane. Methane hydrate floats in water, just as regular ice does. The only thing holding all that methane down in the ocean is the mud it's buried in.

Methane is a powerful enough greenhouse gas that releasing 500 Gton C of it all at once would force the climate equivalently to a 10 times increase in CO₂ concentration, which is a climate forcing more extreme than predicted by even the most aggressive business-as-usual scenario. Fortunately, no one has come up with a mechanism to release that much methane so quickly. If you gave Earth a very good shake, you could do it, but it's hard to shake a whole planet.

Submarine landslides, triggered by melting hydrates producing bubbles in the sediment column, are capable of releasing methane, but these are regional in scale rather than global, and would not release enough methane to really alter the climate. The largest submarine landslide known, called Storegga, off Norway, could have released, as an upper limit, enough methane to increase the atmospheric concentration by 0.5 ppm or so. The

resulting methane spike would have warmed the planet about as much as large volcanic eruption can cool it: significant but not apocalyptic.

Even if the surface of the Earth warmed quickly owing to fossil fuel CO_2 , the temperature change where the hydrates are would be slow, paced by the thousand-year warming time scale of the deep sea and another thousand years to get the heat a few hundred meters into the sediments where the hydrates are. The climate impact of a slow dribble of methane into the atmosphere would be much smaller than that of a sudden catastrophic pulse (see box 5.2, “The Kinetics of a Transient Gas in the Atmosphere”). There would be no way to make landslides around the world all go off within a few years. Instead, global warming would probably trigger many submarine landslides, spread out over centuries. To release a significant fraction of the global methane reservoir would require a landslide of a different order, affecting entire ocean basins—the result of a planetary impact perhaps.

Our model of the hydrate reservoir in the ocean says that if the ocean were a few degrees warmer, in the steady state there would not be much hydrate in the ocean at all (Buffett and Archer 2004). The transient question, what happens when you start from an ocean basin full of hydrate and then raise the temperature, has only started to be accessible to modeling. The most likely outcome is that it will take thousands of years to warm and melt most of the hydrates in the ocean bed. But it's not clear

what the fate of that carbon will be, whether it is to remain as bubbles in the sediment column, to reach and be oxidized in the ocean water column, or to make it into the atmosphere.

The Arctic shelf of Siberia may be a special case. The water column is colder than the global average, so hydrate can be found in water as shallow as 200 meters (as opposed to 500–700 meters elsewhere). The temperature change in the Arctic is amplified by the climate feedback due to melting the ice, so that the Arctic has been warming much faster than almost anywhere else, and it is projected to continue to do so. There is a lot of methane in the Siberian shelf, fed by subsurface “geologic” deposits of thermogenic methane.

There have been many recent reports, in newspapers mostly, of methane bubbles erupting from the seafloor off Siberia and Norway, and there has been 1°C of warming in the water at the Norwegian site. But the overall source of methane from this and all other “geological” sources of methane are small relative to the sources from agriculture and the fossil fuel industry (Denman et al. 2006), and it’s not certain whether the observed methane fluxes are new or have always been there.

The easiest scenario to imagine in the warming of hydrates is for a long, slow, chronic release, raising perhaps the long-term equilibrium methane concentration in the air, but not leading to catastrophic climate spikes from fast releases. Over time, the carbon dioxide product of methane oxidation builds up, and the warming impact of

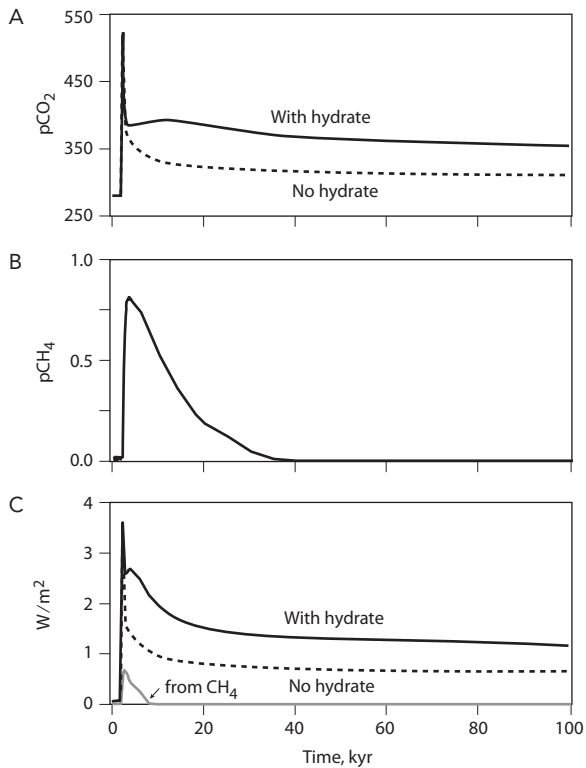


Figure 16. Response of a simple hydrate reservoir model to human CO_2 emissions. (a) Atmospheric $p\text{CO}_2$. (b) Methane. (c) Radiative forcings. (Source: Buffett and Archer 2004)

that long-tail CO_2 is comparable to that of the transient methane (figure 16).

The Paleocene-Eocene Thermal Maximum event is commonly blamed on a catastrophic collapse of the methane hydrate reservoir. However, as mentioned in

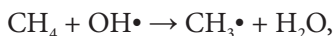
chapter 2, the problem with methane as the source of the carbon is that there wouldn't be enough of it to cause the warming implied by the $\delta^{18}\text{O}$ of CaCO_3 .

Fossil Fuel Industry

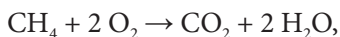
Methane is the dominant constituent in natural gas, one of the three forms of fossil fuel carbon (see box 1.6, "Origins and Inventories of Fossil Fuels"). Methane is also commonly associated with the other two forms, oil and coal. Oil can bubble with methane the way a bottle of beer bubbles with CO_2 when the bottle is opened and the pressure released. Often gas is extracted as a by-product of oil extraction, but it is mined too far away from the gas market to make it worth transporting. Sometimes this "stranded" gas is flared, combusted to CO_2 as it is released, and other times it is just released as methane to the atmosphere. Energy is extracted from any of these fuels by combusting it to CO_2 . However, leaks in the infrastructure guarantee that fossil fuel industry will be a source of methane to the atmosphere as well as of CO_2 .

METHANE DEGRADATION

Most of the CH_4 in the atmosphere will have as its ultimate fate a reaction initiated by hit-and-run attack from a little molecule called OH radical and written $\text{OH}\bullet$ (Jacob 1999). $\text{OH}\bullet$ is a water molecule missing a hydrogen atom and hungry to get that hydrogen back. The hydroxyl radical steals one hydrogen atom from methane,



to make a methyl radical ($\text{CH}_3\bullet$) which is chemically hyperreactive, just as $\text{OH}\bullet$ is. From the methyl radical the carbon is quickly converted by a chain of reactions to carbon monoxide (CO), and then after a couple of days to carbon dioxide (CO_2). The overall reaction is



from the sum of a half-dozen or more such elementary reaction steps.

The lifetime of methane in the atmosphere depends on the concentration of $\text{OH}\bullet$ radical. At night, or trapped in a dark bubble in an ice core, methane can sit in oxygen forever without reacting much, like the stability of an unlit candle. The concentration of $\text{OH}\bullet$ determines the rate at which the atmosphere can cleanse itself of reduced gases such as methane, CO , and hydrocarbons.

It doesn't appear as though the scrubbing intensity of the atmosphere has changed much as a result of human activity, despite our best efforts. The main sinks for $\text{OH}\bullet$ are methane and CO , the concentrations of both of which have doubled owing to human activity. There seems to have been a compensating increase in the sources for $\text{OH}\bullet$, owing to some of the components of urban smog (box 5.4, Methane Radical Oxidation Chemistry).

In deeper geologic time it is interesting to speculate about past biospheres in which methane plays a primary role in climate, the way we think CO_2 does on Earth today. When the atmosphere was anoxic, the lifetime

Box 5.4**Methane Radical Oxidation Chemistry**

Methane is primarily oxidized by reaction with hydroxyl radical, $\text{OH}\cdot$, in a stew of chemical reactions in the troposphere, similar to the chemistry in a candle flame. Additional sinks, accounting for about 10% of the methane, include destruction by ultraviolet (UV) light in the stratosphere and oxidation by bacteria in soils (see table 1).

A radical, as we are using the term here, is defined as a chemical species with an unpaired electron. There is no net charge, the way there would be in water (charged atoms and molecules in water are called ions). In water, you find OH^- , a water molecule sans hydrogen ion (H^+). The $\text{OH}\cdot$ in the air is uncharged because it still has one of the two electrons from the missing hydrogen-oxygen bond. This is an unpaired electron, very energetically unstable and hungry for a hydrogen to bond with.

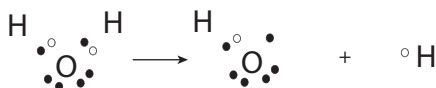
The way to understand radical chemistry is to draw Lewis dot structures. These diagrams sort the outer shell of electrons of each element into chemical bonds, which are shared pairs of electrons between two nuclei, and unshared pairs of electrons, associated with one nucleus only.

As an example, we can start with water. Oxygen has six valence electrons, each hydrogen one. The Lewis structure for water has single bonds between each hydrogen and the oxygen, holding two electrons each. The oxygen also has two unshared pairs of electrons. Oxygen now has eight valence electrons, so it's happy, and hydrogen has two, which is how many it needs (figure 17a).

We can create an $\text{OH}\cdot$ radical by removing one hydrogen and an electron. Radical compounds have odd numbers of valence electrons, if you add them up between all the elements in the compound. Water has eight, $\text{OH}\cdot$ has only seven.

(Box 5.4 continued)

A



B



Figure 17. Free radicals in Lewis dot structure diagrams. (a) Water splits into OH• and H• radicals. (b) The nitric oxide (NO) radical.

The trick to doing Lewis structures of radicals is to determine which of the atoms in the molecule gets the unpaired electron. The rule is that an element that carries a radical will have one fewer chemical bond than it would if it were in a stable, non-radical molecule like H₂O. Oxygen in water has two bonds, each hydrogen one. The unpaired electron must go on the oxygen, leaving a single chemical bond between oxygen and hydrogen. If hydrogen had an unpaired electron, it would not want to be bonded with anything. In fact, there is hydrogen radical in the atmosphere; it's part of the atmospheric radical stew. Another interesting example is the NO radical. See if you can work out why the radical has to be on the nitrogen (figure 17b).

The concentration of OH• is analogous to the brightness of the candle flame, determining how quickly the fuel, methane and oxygen, can be converted to combustion products, CO₂ and water. The lifetime of OH• in the atmosphere is about a second, meaning that the concentration of OH• reaches an equilibrium,

where consumption balances production, very quickly (see box 5.2, "The Kinetics of a Transient Gas in the Atmosphere"). Radicals are produced when UV light from the sun encounters a few specific types of molecules in the air. At night, with no production of radicals by UV, the whole thing shuts down, and the concentration of $\text{OH}\cdot$ goes essentially to zero.

$\text{OH}\cdot$ also cleans the atmosphere of carbon monoxide (CO) and hydrocarbons, such as evaporated gasoline and the isoprene emitted by plants and trees. There are more of all of these molecules in the atmosphere than there used to be, twice as much methane and CO both, so one might have expected the increasing burden to have decreased the concentration of $\text{OH}\cdot$.

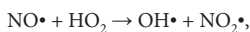
Atmospheric chemists say that the atmosphere has only so much oxidizing power, and that the different compounds in want of oxidation, such as CH_4 and CO , compete for that oxidizing power. Note that they are not talking about thermodynamics (equilibrium), because there is more than enough O_2 in the atmosphere to oxidize all the CH_4 and CO . They are talking about kinetics, the rate at which the reaction can proceed, which is limited by availability of $\text{OH}\cdot$ to catalyze the reactions.

Some pollutants, hydrocarbons and a family of nitrogen compounds called NO_x , act to stoke the fire, increasing the concentration of $\text{OH}\cdot$ and making everything burn faster. $\text{OH}\cdot$ is not the only radical chemical species in the atmosphere: it is part of an intricate web of reactions between a half dozen or so main other radical players.

Most of the business of atmospheric chemistry is accomplished by catalytic cycles involving interreacting families of radical compounds such as one called NO_x . This family consists of two compounds, $\text{NO}\cdot$ and $\text{NO}_2\cdot$. Both of these are radical; N brings five valence electrons and O brings six, so the total is odd for both of these compounds.

(Box 5.4 continued)

NOx catalyses a pathway of reactions that results in production of more radicals. In clean air, one sink for radicals, a way for the flame to wash out, is for a radical compound HO₂ to form hydrogen peroxide (H₂O₂) and dissolve into rainwater. Instead of allowing this to happen, NO• steals an oxygen from HO₂, leaving OH• radical and NO₂•:

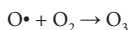


thus keeping the radical flame alive.

NO₂• has the distinction of being able to absorb UV sunlight in the lower atmosphere, where the UV is not very intense. When NO₂• absorbs light, it splits (“photolyzes”) back into NO• plus an oxygen atom:



in effect absorbing the UV to split one radical into two. (The oxygen atom is the exception to rule of odd electrons = radical; it has six outer shell electrons, an even number, but an incomplete outer shell, so it behaves as a radical.) The only other molecule able to absorb UV light in the troposphere is ozone, O₃. The fate of the oxygen atom is to react with oxygen:



to make ozone. The NOx family not only preserves radicals from washing out, it also creates molecules that absorb UV energy to create new radicals. The human release of NOx and the resulting higher concentration of ozone in the troposphere could potentially stoke the fire of the atmosphere, decreasing the lifetime of methane.

The NOx family is one primary ingredient for making ozone in urban air. The other ingredient is hydrocarbons, the oxidation of which supplies the thermodynamic gradient

down which all of these spontaneous chemical reactions are surfing. Controlling urban ozone requires limiting whichever ingredient, NO_x or hydrocarbons, is in shortest supply. In most places, natural emission of hydrocarbons by trees is enough that the chemistry is said to be NO_x-limited, so cutting NO_x pollution has more effect on local ozone than cutting hydrocarbon pollution does.

It has only recently become possible to measure the concentration of OH• directly, and this sort of measurement would be difficult to scale up to an average or inventory over the entire atmosphere such as we would need to calculate the lifetime of CH₄, because OH• varies so wildly and quickly with conditions (sunlight, for example). But there are indirect measurements of the total amount and activity of OH• in the air, for example how quickly a human-released compound methyl chloroform (CH₃CCl₃) decomposes, or the concentration of the carbon-14 age of carbon monoxide (CO), which also meets its end by chance encounter with OH•.

These indirect measurements of the oxidation rate (flame intensity) of the atmosphere seem to indicate that the atmosphere is not burning much brighter or dimmer than it was a few decades ago. The lifetime of methane in the atmosphere appears to have been fairly stable. It seems as though, more or less by chance, the acceleration of methane decomposition owing to increasing NO_x and ozone, just about balances the slowing of methane decomposition owing to the standing-in-line effect from increasing methane and CO. The future stability of the methane oxidation chemistry is impossible to predict with any confidence. We are just lucky that the system has been as stable as it has.

Further reading: Jacob 1999.

of methane may have been thousands of years, allowing much higher concentrations to build up.

Climate geochemists have even discussed the possibility of a temperature-regulating mechanism similar to the weathering CO_2 thermostat but involving methane, which might have been active on early Earth (Kasting, Pavlov, and Siefert 2001; Pavlov et al. 2000). This would be an auxiliary thermostat to the CO_2 mechanism; ultimately Earth's climate would seek a condition that would satisfy both thermostats. With warm temperatures on Earth supported by methane, the CO_2 concentration of the air could drop, until the rate of weathering became limited by CO_2 availability just enough to balance the rate of CO_2 degassing from the Earth.

One proposed explanation for the snowball Earth event (see chapter 2) is that methane played a role in the planetary thermostat, but was unstable to the rise of atmospheric oxygen. If the methane concentration of the air dropped abruptly, there wouldn't be enough time for CO_2 to build up enough to prevent Earth from falling into the snowball. Once the new climate state is locked in, it takes millions of years and monstrously high atmospheric CO_2 concentrations to finally unlock the world from all that ice.

Here is one idea for a methane thermostat. Methane is produced biologically, but life suffers and slows down if the temperature gets too high. So perhaps methane could be viewed as a waste product of early life that built up until the climate pushed the temperature tolerance of the methane producers.

Here is another idea. On Saturn's moon, Titan, methane in the air degrades in the upper atmosphere into organic molecules that form a haze of tiny suspended droplets. These organic aerosols reflect incoming visible sunlight, cooling the planet. Perhaps methane in the atmosphere of the early Earth built up to a high enough concentration to start forming this haze, which then slowed down the rate of biological methane production by cooling things down too much.

PRESENT AND FUTURE OF ATMOSPHERIC METHANE

The methane concentration in the air today is about 1.6 ppm, double the 0.7 ppm of the natural atmosphere from ice core samples dating to around the year 1750. Relative to the year 1750, methane accounts for about half of the climate forcing from the higher CO₂ concentration. Given the state of our understanding of the present and recent past, it is pretty useless to try to predict the future of methane and its influence on climate in detail. However, since methane is a transient gas while CO₂ accumulates, there is probably greater potential for atmospheric CO₂ to rise than there is for methane.

The rise in atmospheric methane has been driven primarily by an increase in the anthropogenic sources described above. In spite of our expectations that the lifetime of methane ought to have increased due to limited amounts of hydroxyl radical (OH•) to react with, other human impacts on the chemistry of the atmosphere have

stimulated $\text{OH}\cdot$ production just about enough to keep up with demand.

The concentration rose for decades, but came to an abrupt plateau in about the year 1993 (figure 18) (Dlugokencky 2003). From then until just about 2007, the concentration in the air remained relatively steady. Why did it stop going up? One possibility is that the source flux since about 1985 or so was holding steady, not increasing, and the concentration reached its steady-state value in 1993. Another possibility is that there was an actual decrease in methane emission around 1993, stopping the previous rise in its tracks. The beginning of the methane plateau coincided in time with the collapse of Eastern Europe, perhaps pointing to the Russian fossil fuel industry or other economic activity of the Eastern European bloc. Another possibility is that increases in human emission of methane are being masked by anomalous dryness globally, decreasing the natural methane fluxes from swamplands.

Beginning in the year 2007, methane seems to have restarted its upward climb (Dlugokencky 2009). Previous one-year wiggles in the methane concentration were easy to explain in terms of the El Niño climate cycle, as it affects the soggyiness of the swamps. But this most recent upturn in methane concentration is still mysterious. There have been reports in the scientific literature and in the newspapers of plumes of methane erupting from Arctic lakes and the Siberian Shelf, but these sources are generally small relative to the known natural and artificial sources listed in table 1.

We are left with a picture of the methane cycle too poorly characterized and understood to really make any

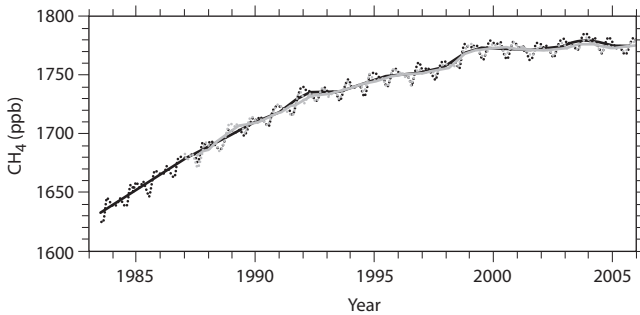


Figure 18. Recent history and rate of change of atmospheric methane concentration. (Source: Dlugokencky 2003)

predictions about the future. Methane has a huge potential to alter the climate, given its potency as a greenhouse gas, and the large inventories of methane stored in the oceans, and the potential to make methane from the frozen peats in Arctic permafrosts.

The geologic past is full of severe disruptions to the climate and carbon cycle, and methane often gets invoked as a usual suspect, but not much has been proved. For what reassurance it's worth, however, no one has proposed a way for methane to suddenly erupt in a climate-game-changing way in our immediate future, nor has anyone observed anything that looks like the beginning of such a calamity. By contrast, observations of ice flow at the edges of ice sheets do look like the first pages of a disaster novel.

People ask me if they should be especially worried about methane. I tell them there's plenty to worry about from human-released CO₂.

6 SUMMARY

The prognosis for the future of the carbon cycle is clear enough to muddle through the next decade or so, but for the coming century and longer the carbon cycle is a loose cannon on deck, conceivably capable of doubling the human impact on climate.

THIS BOOK, A PRIMER ON THE ROLE OF THE CARBON cycle in Earth's climate, has been 80% about CO₂. The concentration of CO₂ in the atmosphere is a critical variable in the carbon cycle and in the energy budget of the Earth. The carbon cycle of the biosphere is what is known as an "emergent phenomenon," a complex dance among interrelated elements that would have been impossible to predict or anticipate in advance. If somehow we'd never heard of life, who would have thought of it, or imagined it possible? Especially amazing is that the biosphere, complex beyond imagining, appears to have found an intrinsic stability, controlling vital statistics of the Earth's surface, including temperature, oxidation state, and the concentrations of various biologically important nutrient elements.

There have been sweeping changes in Earth's climate in the past, driven by the peculiarities of the weathering CO_2 thermostat as tweaked by the arrangement of continents, the uplift of mountain belts, and sediments going into subduction zones. The climate of Earth drifts back and forth between icy climates such as ours and hothouse worlds with tropical conditions to the poles. The available stocks of fossil fuels are probably sufficient to drive Earth back to a hothouse climate regime, at least for a while.

There have also been meltdowns and breakdowns of stability in Earth's history. Biological evolution is marked by five great extinctions, with our own time becoming potentially a sixth. Isotopic records of carbon-13 and oxygen-18 preserved in CaCO_3 sediments tell of carbon cycle meltdowns, such as the Paleocene-Eocene Thermal Maximum and the purported snowball Earth event. So far, at least, the Earth has always recovered from these sudden twists and collapses, and on the time scale of the age of the Earth, it recovers quickly. From our own point of view, however, in our limited life spans, the "long tail" of the global warming climate event, a property of the weathering CO_2 thermostat, appears to be essentially forever.

The carbon cycle switches sides as we consider different time scales. It stabilizes the climate over millions of years but amplifies the climate swings of the glacial cycles. Today the carbon cycle is absorbing fossil fuel CO_2 , damping down the climate swing. But on longer time scales it is reasonable to fear that the carbon cycle could

begin to release CO_2 into the atmosphere in response to a warming climate. There are several carbon reservoirs that could potentially respond in this way, amplifying the global warming climate event.

On the shortest time scales, we should look perhaps to tropical rain forests such as the Amazon, which could dry out and burn catastrophically. Fire could take the peat deposits in Indonesia. One could imagine tens or even 100 Gton C released in a few years by such a mechanism, spiking atmospheric pCO_2 upward, maybe releasing as much carbon as we do.

The other carbon reservoir to watch on land is the permafrost peat deposits. Frozen peats are most abundant in high northern latitude areas that have never been glaciated, with Siberia a prominent example. Organic carbon in peats has been protected from degradation for millennia by being frozen, but it begins to degrade immediately upon melting. There are also methane hydrates in some permafrost soils, which could potentially release methane along with the peat degradation gases. There are hundreds of Gton C in the permafrost peat and hydrates. These are likely to release carbon slowly, on a time scale of centuries.

The oceans appear to have been the main player in the positive carbon cycle feedback through the glacial cycles. Atmospheric pCO_2 changes recorded in ice cores generally took a thousand years or longer, consistent with the equilibration time scale between the atmosphere and the ocean. Presumably, a positive feedback originating from the ocean in the future would also take a thousand years

to really kick in. But it's unclear what the mechanism was that drove the CO_2 variations through the glacial cycles, so it is impossible to say whether that same mechanism could go in the opposite direction if it were warmed further, releasing even more CO_2 .

Methane hydrates in the ocean would release carbon very slowly, paced by the thermal inertia of the ocean and the diffusion time of heat into the sediments where the hydrates are. If melting hydrates someday trigger a submarine landslide, it will seem catastrophic to the beachgoers where the tsunami hits, but as a release of methane to the atmosphere the landslide cannot be large enough to be called catastrophic. A slow, chronic release of methane to the atmosphere could raise the concentration of methane to a new, higher steady state, while the CO_2 oxidation product of the methane will accumulate in the carbon cycle the same as fossil fuel CO_2 does. The hydrates are an ominous carbon reservoir, in that the climate of the Earth could be warmer in the near future than it has been for millions of years, all the while the methane has been accumulating.

If ever there was a time in Earth's history for a strong carbon cycle feedback, now would be it. The hydrate, peat, and rain forest carbon reservoirs are probably about as charged up with carbon as they ever get. Earth's climate of the past few million years has been particularly unstable, dominated by the quirky life cycles of the Northern Hemisphere ice sheets. And human industry is poking the carbon-climate system very strongly, by releasing so much carbon so quickly. Maybe the carbon

reservoirs are like a bundle of TNT and fossil fuel combustion is like a sharp detonator, able to coax an explosion out of ingredients that might otherwise be stable.

It is premature even to attempt to guess how strong the overall carbon cycle feedback on climate might be, but my hunch is that, in the worst-case scenario, the carbon cycle feedback might eventually release as much CO₂ as humans do, a sort of natural “matching funds” arrangement. If the carbon cycle feedbacks in general were much stronger than that, the climate system would be so unstable it would have melted down in the geologic past more frequently than it apparently has. But Earth’s biosphere and carbon cycle are vastly more creative than human imagination is able to anticipate, so don’t take my word for any of this. We’ll have to wait and see.

Glossary

Abrupt climate change—a climate flip-flop in just a few years from one state to another. The new state can last for hundreds of years or longer.

Acid—a molecule that releases protons, H^+ ions, to a water-based solution.

Activity coefficient—a fudge factor in thermodynamics that corrects the ideal availability of a chemical, based on its concentration, for molecular interactions that alter its availability. An activity coefficient of 1.0 would be the ideal approximation.

Alkalinity—the concentration of compounds in water that would react with acid if it were available. See box 3.1, “Carbonate System pH Chemistry.”

Amino acids—the building blocks of proteins. See box 1.5, “Biochemistry 101.”

Anthropocene—the geologic time interval in which humans played a dominant role in the chemistry of the Earth.

Apparent thermodynamic constants—equilibrium constants that have been corrected for the activity coefficients of the chemical species in a reaction.

GLOSSARY

Aragonite—mineral form of CaCO_3 , more soluble than its cousin mineral calcite, which shares the same chemical formula.

Archaea—primitive branch of the tree of life. Archaea look like small bacteria.

Base—chemical that produces OH^- ions when added to a water solution.

Bicarbonate— HCO_3^- , the neutral form of the carbonic acid family in water.

Biogenic methane—methane produced by living things.

Biological pump—the chemical impact of plankton growing in the surface ocean and decomposing in deeper water.

CaCO_3 pH-stat—the pH-governing effect of the CaCO_3 cycle.

Calcite—mineral form of CaCO_3 , chemical cousin to aragonite.

Carbohydrates—organic compounds with chemical formulas similar to CH_2O , including sugars and starches.

Carbonate ion— $\text{CO}_3^{=}$, the basic or high-pH form of the carbonic acid family.

Carbonic acid— H_2CO_3 , the acidic form of the carbonic acid chemical family.

Clay minerals—left behind when igneous rocks weather, they form soils.

Coccolithophorids—class of marine phytoplankton that make shells of little plates of CaCO_3 .

Continental shelves—rings around many of the continents on Earth with water depth of around 100 meters or less.

Daansgaard-Oeschger event—1,500-year climate cycle with abrupt warming during the last glacial time, as revealed in Greenland ice cores.

Diatoms—class of marine phytoplankton that make shells out of SiO_2 .

Dissociation—separation of an acid into an H^+ and its negative other part, like HCO_3^- .

Eddy correlation CO_2 flux measurement—a method of estimating the vertical flow of CO_2 above the land or ocean surface by correlating vertical velocities and CO_2 concentrations.

Equilibrium—thermodynamic lowest energy state of a chemical system.

Euphotic zone—sunlit zone in the surface ocean where photosynthesis is possible.

Faint young sun paradox—the question of how the Earth has remained nearly constant in its temperature even as the sun has gradually warmed.

Fennoscandian ice sheet—ice sheet that covered northern Europe during glacial times. It does not exist today.

Global warming potential—a way of comparing the climate impacts of different greenhouse gases, taking into account their lifetimes.

H₂CO₃*—chemical shorthand for the sum of dissolved CO₂ gas in water plus hydrated CO₂ gas, H₂CO₃, used in thermodynamic calculations.

Heinrich events—a class of abrupt climate changes during glacial times, driven by the Laurentide ice sheet periodically collapsing into icebergs in the North Atlantic.

Henry's law constant—the solubility of a gas, for example CO₂, expressed as the partial pressure in the air divided by the equilibrium H₂CO₃* concentration in the solution.

Holocene—interglacial climate of the last 10,000 years.

Hydrocarbons—organic carbon molecules composed mostly of CH₂ chains, not to be confused with carbohydrates, which are composed of CH₂O.

Hydrophilic—dissolves in water.

Hydrophobic—does not mix with water (such as oils).

Ion—charged atom or molecule.

Laurentide ice sheet—major ice sheet covering North America during glacial times. It does not exist today.

Lipids—hydrocarbon biomolecules that provide structure to cell walls and store energy.

Metabolic carbon—in the ocean, the dissolved CO_2 associated with plankton growth and decay, correlated with nutrient concentrations according to the Redfield ratio.

Micromolar—moles of solute per liter of solution multiplied by 1 million.

Missing sink—a hole in the carbon budget; it must be on land somewhere.

Molar—moles of a solute per liter of solution.

Mole—equal to $6.02 \cdot 10^{23}$ atoms or molecules. A mole weighs the atomic weight of the elements in grams.

Nitrate— NO_3^- , a major nutrient in the ocean.

Nutrients—elements required for photosynthesis.

Oil source rocks—sedimentary rocks with high organic carbon concentrations that can form oil.

Orbital forcing of climate—variations in the intensity of the sun according to latitude and season that drive climate changes.

pCO_2 —partial pressure of CO_2 , equal (ideally) to the total pressure times the molecular fraction of CO_2 . The pCO_2 of a water sample is defined as the pCO_2 of a hypothetical air parcel in equilibrium with it.

Peat—swamp deposits rich in organic carbon.

pH—negative log of the H^+ activity in a water sample. Low pH is acidic and high pH is basic.

GLOSSARY

Phosphate— PO_4^{3-} , a major nutrient in the oceans.

Phytoplankton—microscopic algae in the ocean.

Polar front—a boundary in the ocean around Antarctica demarcating the cold dense nutrient-rich waters to the south from the nutrient-depleted waters to the north.

Radical—an atom or molecule with an unpaired electron, found in the gas phase and responsible for most atmospheric chemistry reactions.

Redfield ratio—a canonical ratio of the constituents of phytoplankton in the ocean, most recently taken to be $\text{C}_{125}\text{N}_{16}\text{P}_1$.

Silica—chemical form of dissolved silica can be written as H_4SiO_4 (hydrated) or SiO_2 (unhydrated). The solid form used by phytoplankton to make shells is amorphous (non-crystalline) SiO_2 .

Solubility product—an equilibrium constant describing the solubility of a mineral.

Sphagnum—type of moss associated with peat.

Sugars—rings of carbohydrate.

Thermogenic methane—methane produced abiologically, by cooking.

Total CO_2 —computed quantity for sea water chemistry, equal to the sum of the dissolved carbonic acid family species, $\text{H}_2\text{CO}_3^* + \text{HCO}_3^- + \text{CO}_3^{=}$.

Tracer—chemical measurement in the ocean used to figure out how the water is flowing, in particular from the surface to the deep.

Weathering CO₂ thermostat—feedback mechanism that stabilizes Earth's climate on time scales of millions of years.

ΣCO₂—see *Total CO₂*.

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