

# 1 CARBON ON EARTH

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## 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

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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<sub>2</sub>) release take place in the context of three grand stabilizing feedback systems in the global biosphere carbon cycle: the weathering CO<sub>2</sub> 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<sub>2</sub> thermostat, which stabilizes Earth's climate by regulating the CO<sub>2</sub> concentration in the atmosphere (see chapter 2). The idea is that the rate of chemical weathering, which results in carbon sequestration as calcium carbonate

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**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  $6.02 \times 10^{23}$  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  $\text{CO}_2$  (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

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*(Box 1.1 continued)*

mass of carbon alone and the mass of CO<sub>2</sub>, including the oxygen atoms. Some people talk about the costs of reducing CO<sub>2</sub> emissions in dollars per ton of carbon, others in dollars per ton of CO<sub>2</sub>; 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 CO<sub>2</sub>.

I think of the conversion factor as equivalent to the statement that 44 g CO<sub>2</sub> 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 CO<sub>2</sub>/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.

(CaCO<sub>3</sub>) in sedimentary rocks, increases as a function of temperature, pulling the CO<sub>2</sub> 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

CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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

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*(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  $\text{CO}_2$ , carbonic acid ( $\text{H}_2\text{CO}_3$ ), bicarbonate ion ( $\text{HCO}_3^-$ ), and carbonate ion ( $\text{CO}_3^{2-}$ ). These chemical forms of carbon are oxidized, just as  $\text{CO}_2$  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 ( $\text{CaCO}_3$ ) and organic carbon, mostly in the form of a random indescribable goo called kerogen. 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  $\text{CO}_2$  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  $\text{CO}_2$  thermostat,

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**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  $\text{CO}_2$  and methane ( $\text{CH}_4$ ) 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  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{CH}_2\text{O}$ .

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  $\text{CaCO}_3$  between sedimentary rocks and the ocean (Broecker and Takahashi 1978).  $\text{CaCO}_3$ , 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  $\text{CaCO}_3$  that flows into and out of the ocean. The input is from the dissolution of land rocks, including  $\text{CaCO}_3$ -containing rocks, a geochemical reaction weathering, and the output is in the form of  $\text{CaCO}_3$  deposition on the seafloor. The ocean pH must be right for sedimentation to balance weathering, and as the ocean balances its  $\text{CaCO}_3$  budget, it controls the ocean pH. This mechanism, called the  $\text{CaCO}_3$  pH-stat, takes a few thousand years to adjust the ocean’s pH, faster than either the weathering  $\text{CO}_2$  thermostat (100,000 years) or the oxygen homeostat (2 million years) (see chapter 4).

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## 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  $\text{CO}_2$  from the atmosphere at a significant rate, reducing the climate impact of our releasing that  $\text{CO}_2$ . 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  $\text{CO}_2$  thermostat mechanism regulates the atmospheric  $\text{CO}_2$  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  $\text{CO}_2$  degassing from the Earth in volcanic gases and deep-sea hydrothermal vent fluids (Walker, Hays, and Kasting 1981).

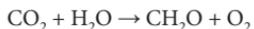
The set-point of the  $\text{CO}_2$  thermostat can be tweaked, like changing the target temperature of a house's thermostat. Any change in the processes of chemical weathering or  $\text{CO}_2$  degassing can alter the set-point of the

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**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  $\text{CH}_2\text{O}$  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  $\text{CO}_2$  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  $\text{CO}_2$ , cooling the planet until the rate

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of chemical weathering falls back into balance with CO<sub>2</sub> degassing from the Earth.

If the rate of CO<sub>2</sub> emission from the Earth were higher at some point in the past, it would have pushed atmospheric CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> concentration in bubbles of ancient atmosphere trapped in polar ice. The measurements showed that the CO<sub>2</sub> 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

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a glacial time, and the lowered  $\text{CO}_2$  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  $\text{CO}_2$  cycles that would account for at least the direction of the response is based on the solubility of  $\text{CO}_2$  in water. Cooler water can hold more  $\text{CO}_2$  than warm water can, so when the Earth cools down, more  $\text{CO}_2$  would dissolve in the cooler ocean. However, as will be described in detail in chapter 3, the  $\text{CO}_2$  cycles are stronger than can be explained by this mechanism alone. In fact, it's not clear what drives the glacial  $\text{CO}_2$  cycles.

The glacial cycles are shorter than the response time scale for the weathering  $\text{CO}_2$  thermostat, so it is as if, in a house, an intermittent sunbeam coming in a window

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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  $\text{CH}_2$  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  $\text{CH}_2$  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

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(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 CO<sub>2</sub> emissions into the oceans and the land's surface. The carbon cycle is moderating the climate impacts of our CO<sub>2</sub> 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 CO<sub>2</sub> 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

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**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 ( $\text{SO}_4^{2-}$ ), which is reduced to sulfide ( $\text{H}_2\text{S}$ ) 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 sub-surface Earth, at temperatures of ca.  $300^\circ\text{C}$  for tens of millions of years. With a chemical formula  $\text{C}_n$ , 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 ( $\text{CH}_4$ ). 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  $\text{CaCO}_3$ , silica ( $\text{SiO}_2$ ), 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 ( $-161^{\circ}\text{C}$ ) is much lower than for its higher-C cousins, propane ( $-43^{\circ}\text{C}$ ) and butane ( $-0.6^{\circ}\text{C}$ ).

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:

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

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*(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:

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

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

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

CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> emissions.