

## CHAPTER 2

# Atmospheric Structure and Composition

### CHAPTER AT A GLANCE

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The *atmosphere* is a collection of gases held near the Earth by gravity. It is also pulled away from the Earth because a vacuum exists in the harsh conditions of space. One of the most fundamental properties of the universe—the **second law of thermodynamics**—states that energy (and, therefore, mass, because energy and mass are related by Einstein's theory of relativity) moves from areas of higher concentration (in this case, Earth's lower atmosphere) to areas of lower concentration (outer space). The atmosphere thus represents a place where a balance is generally achieved between the downward-directed gravitational force and

the upward-directed force of buoyancy. This balance is termed **hydrostatic equilibrium**. This extremely thin and delicate zone known as the atmosphere makes life as we know it possible on the planet. When you look in the sky the atmosphere appears to continue infinitely, but if Earth were the size of an apple, the atmosphere would have the thickness of the apple's skin.

Technically, the atmosphere is a subset of the air because it is composed solely of gases. By contrast, air contains not only gases but also **aerosols**—solid and liquid particles suspended above the surface that are too tiny for gravity to pull downward. Solid aerosols include

ice crystals, volcanic soot particles, salt crystals from the ocean, and soil particles; liquid aerosols include clouds and fog droplets.

Because the atmosphere is composed of the lightest elements gravitationally attracted to the Earth, many assume that it has little or no mass. Compared with the mass of the solid Earth ( $6 \times 10^{24}$  kg; or  $6 \times 10^{21}$  metric tons) and oceans ( $1.4 \times 10^{21}$  kg; or  $1.4 \times 10^{18}$  metric tons), the atmosphere is indeed light. But the atmosphere has a substantial total mass of  $5 \times 10^{18}$  kg ( $5 \times 10^{15}$  metric tons)!

The mass of the air is in constant motion, giving considerable impact to the surface environment. For example, a tornado can cause catastrophic devastation to a location. In the case of a tornado, the mass of air has substantial acceleration. According to **Newton's second law of motion**, force is the product of mass and acceleration. The two factors combine, in this situation, to produce a force capable of devastation.

The atmosphere is an extremely complex entity that must be viewed simultaneously on many levels, both temporally and in three spatial dimensions (west–east, north–south, and vertical). Atmospheric processes can be difficult to understand. To appreciate the nature of the atmosphere properly, we must first understand the origins of the atmosphere and its changes since the origin of the planet.

## ► Origin of the Earth and Atmosphere

According to the best scientific information, the universe is thought to have begun 13.8 billion years ago. At that time all matter in the universe was confined to a single space. An explosion of unimaginable proportion sent this matter—mostly hydrogen—outward in all directions. Over time, gravity caused matter to collect in various areas of space to form galaxies. Within the galaxies smaller amounts of matter condensed gravitationally into stars. Star formation began to occur when hydrogen was compressed under its own gravitational weight. If the mass involved was sufficiently large, **nuclear fusion**—a process that converts lighter elements (principally hydrogen) into heavier elements (primarily helium)—began. Such reactions released amazing quantities of radiant energy while creating (fusing) all matter heavier than hydrogen.

Occasionally, a star exploded, sending heavier elements outward through the galaxy. Vast clouds of dust, called **nebula** (FIGURE 2.1), formed, and the original gravitational accumulation process began anew. Our solar system is believed to have formed from a nebula approximately 5 billion years ago. The Sun gravitationally



**FIGURE 2.1** The Orion Nebula.

Courtesy of NASA, ESA, M. Robberto (Space Telescope Science Institute/ESA), and the Hubble Space Telescope Orion Treasury Project Team.

attracted the bulk of the elements that composed the nebula. Planets formed as balls of dust gravitationally collected over various orbits about the primitive Sun. Earth was one such ball of dust. As it grew the elements fused together and collapsed under their own weight and gravity. As Earth grew in size, its gravity increased proportionately. Friction caused the Earth materials to melt. Melting was also encouraged by frequent impacts with large **planetesimals**, which were essentially small planets of condensed debris moving over wildly eccentric orbits about the Sun. These planetesimals contributed heavier elements and mass to the growing Earth while shattering and melting its hot surface. A collision between Earth and a planetesimal is thought to have created the Moon. Remnants of early solar system planetesimals are present today in the vast asteroid field between Mars and Jupiter. The **Oort cloud**—a collection of icy comets and dust that surrounds the outer edges of our solar system—also acts as a relic of conditions present in the early stages of solar system formation.

In these early times Earth's atmosphere is believed to have consisted of light and inert (noble) gases such as hydrogen, helium, neon, and argon. These gases were effectively swept away as the **solar wind**—radioactive particles from the Sun moving through space at nearly the speed of light—developed. Today, Earth is largely devoid of noble gases as a result. So how did the atmosphere that we know today form?

The composition of the atmosphere can be explained by looking at volcanic activity, which is rather limited over Earth's surface today but was apparently widespread

billions of years ago as the early Earth cooled slowly from its primordial molten state. As volcanic material cooled, gases were released through the process of **outgassing**, which primarily involved diatomic nitrogen ( $N_2$ ) and carbon dioxide ( $CO_2$ ), with lesser amounts of water vapor, **methane** ( $CH_4$ ), and sulfur. The **condensation** of water vapor into liquid water in the cool atmosphere formed clouds and precipitation. Precipitation collected in low-elevation areas of the planet and accumulated over time to form the oceans.

Our planet is unique in the solar system because of the presence of liquid water. This is a consequence of many related, and interacting, factors—some of which include distance to the Sun and atmospheric composition. Because water is essential to life, it is not surprising that Earth is the only planet known to support life.

## ► Atmospheric Composition

Today, the dry atmosphere consists primarily of  $N_2$  and diatomic oxygen ( $O_2$ ). Diatomic nitrogen is a stable gas that comprises 78% of the present-day atmospheric volume (**TABLE 2.1**). The abundance of  $N_2$  has increased as a percentage of the total atmospheric volume primarily because it is not removed as effectively from the atmosphere as are most other atmospheric gases. The **residence time**—the mean length of time that an individual molecule remains in the atmosphere—of  $N_2$  is believed to be approximately 16.25 million years.

The next-most abundant gas in the present-day dry atmosphere is oxygen, comprising approximately 21% of the atmospheric volume. About 0.93% of the remaining 1% of the dry atmosphere is composed mostly of argon (Ar), and a wide array of atmospheric trace gases constitute the remainder. Of these,  $CO_2$  is the fourth-most abundant gas in the dry atmosphere, representing 0.041% of the dry atmosphere, or 407 parts per million (ppm), as of June 2016. It plays an especially important

role in maintaining the temperature of the planet at a level comfortable for life in its present form. Earth's early atmosphere apparently contained far more  $CO_2$  than today's and little or no  $O_2$ . So where did most of the  $CO_2$  go after outgassing in the primitive atmosphere, and how did  $O_2$  come to replace it?

The evolution of Earth's atmospheric composition (including  $O_2$ ) involves significant interactions with the *biosphere*, *hydrosphere*, and *lithosphere*. About 3.5 billion years ago an interesting development occurred in the extensive waters of primordial Earth that profoundly affected the evolution of the atmosphere. Single-celled organisms, called **prokaryotes**, began to appear. These simple ancestors of bacteria and green algae absorbed nutrients directly from the surrounding environment. Prokaryotes released  $CO_2$  to the atmosphere as a byproduct of **fermentation**, the process by which simple organisms acquire energy through the breakdown of food. The evolution of prokaryotes led to more complex, often multicellular, organisms called **eukaryotes**, which contain more complex internal structures and release even more  $CO_2$  into the atmosphere in the process of **respiration**. Most life on Earth is believed to have evolved from the further development of eukaryotes. Prokaryotes and eukaryotes would have had to develop in the oceans, however, because without oxygen in the atmosphere the protective **ozone** ( $O_3$ ) layer could not have formed to protect terrestrial life from the harmful **ultraviolet (UV) radiation** emitted by the Sun. Over time,  $CO_2$  continued to accumulate, as it became a larger and larger component of the atmospheric volume.

By about 3 billion years ago another major development in the history of life on Earth apparently caused another major change to the atmospheric composition. The early evolution of eubacteria, and later, protists, and eventually aquatic green plants led to a significant extraction of  $CO_2$  from the atmosphere in **photosynthesis**—the process by which green plants use sunlight to synthesize food.  $O_2$  is released into the atmosphere as a byproduct of photosynthesis. As green plants began to populate Earth, first in the oceans and later on land after the presence of  $O_2$  gradually led to the formation of ozone ( $O_3$ ) and the  $O_3$  layer—atmospheric  $CO_2$  decreased in concentration while atmospheric  $O_2$  simultaneously increased. Today most of the atmospheric  $CO_2$  is stored in vast quantities of sedimentary rock, originally extracted from the atmosphere by living things. The amount of atmospheric  $O_2$  present today represents a similar percentage to that of  $CO_2$  in the early atmosphere.

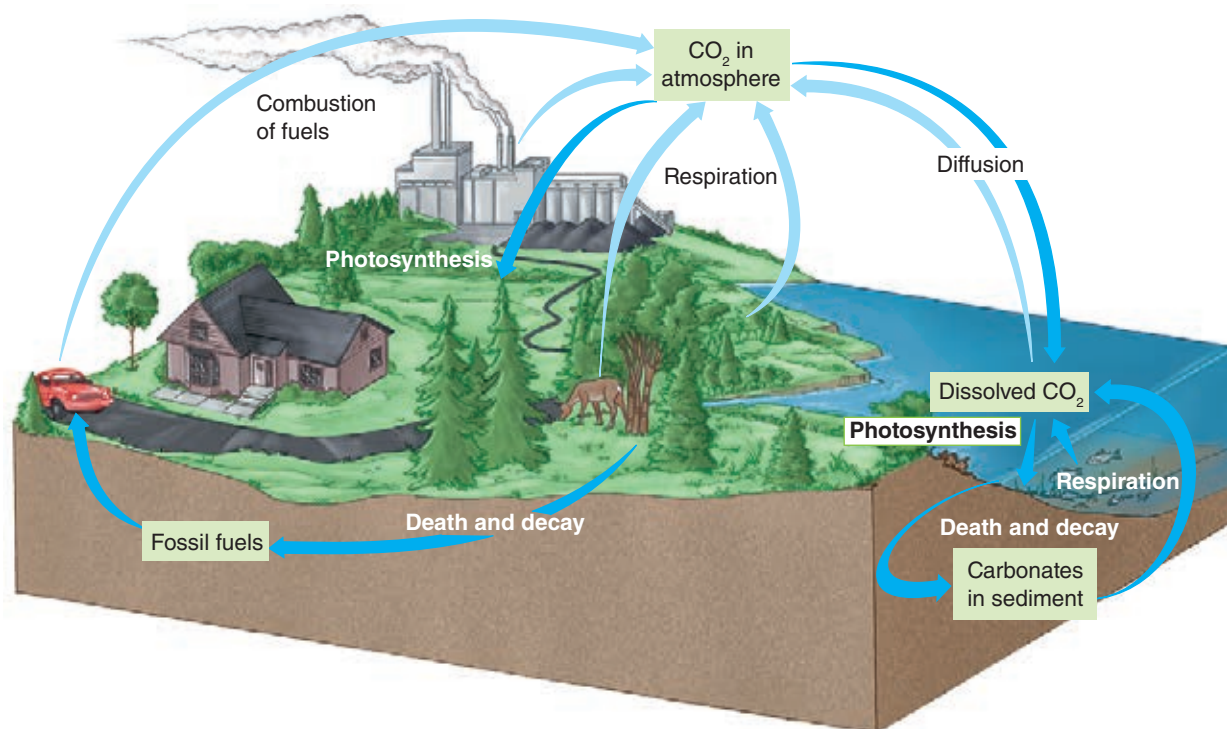
**TABLE 2.1** Composition of the Dry Atmosphere

Gas	Percentage of Air
Nitrogen ( $N_2$ )	78.08
Diatomic oxygen ( $O_2$ )	20.95
Argon (Ar)	0.93
Carbon dioxide ( $CO_2$ )	0.041
All others	0.003

## Carbon Cycle

The process described above essentially represents the atmospheric component of the **carbon cycle**, the





**FIGURE 2.2** The global carbon cycle.

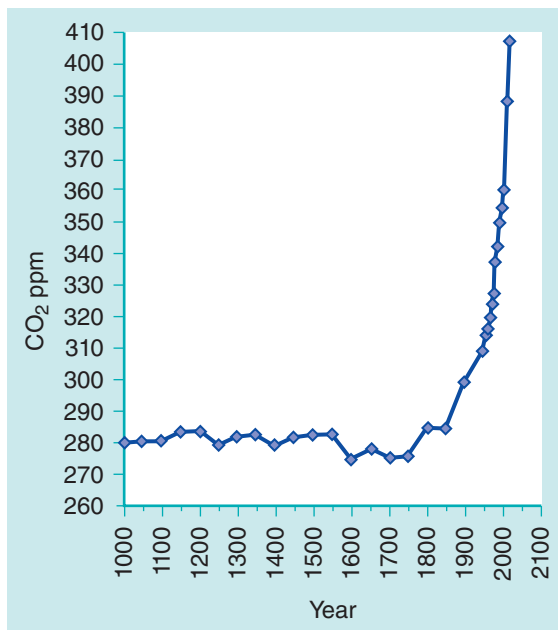
continuous movement of carbon through the Earth–ocean–atmosphere system. Carbon can exist in various Earth–ocean–atmosphere **reservoirs**—the components of a system that effectively store matter and/or energy for a certain period of time, after which they allow for the movement (**flux**) of that matter and/or energy to another component of the system. Carbon reservoirs include the atmosphere, which houses CO<sub>2</sub>; the biosphere, which comprises all living matter; and the oceans, which include dissolved carbonates (**FIGURE 2.2**). Over time carbon cycles among these various reservoirs. The carbon residence time is different for each reservoir, with the rates of exchange directly related to the size of the reservoir. The largest carbon reservoir, comprising the vast majority of carbon in the Earth–ocean–atmosphere system, is sedimentary rock, which may store carbon for billions of years.

The second-largest reservoir is the oceans, which act as a **sink** for atmospheric CO<sub>2</sub> by absorbing many gigatons of CO<sub>2</sub> from the atmosphere each year. Over time CO<sub>2</sub> is transported from the atmosphere into the deep ocean layers in a slow process. Once the CO<sub>2</sub> is transported into the deep ocean, it may remain there for many thousands of years.

The biosphere (including soil) is also a reservoir that acts as a sink for CO<sub>2</sub> from the atmosphere. It is then transported and stored elsewhere in the system. For example, the vast majority of carbon in the rock reservoir was extracted from the atmosphere through

biological processes. Residence time associated with the biosphere may be examined on a number of levels. Carbon is held directly in the biosphere as long as the living organism remains alive. Once the organism dies, carbon exits this sink as the remains of the organism decay. Some of this carbon may become buried naturally and transported into the rock reservoir. This process is effective in marine environments where an abundance of organic matter filters to the ocean floor, building huge layers of organic matter over time. Some of the decaying carbon dissolves directly into water, becoming part of the oceanic carbon reservoir, and some reenters the atmosphere through **diffusion**. Much oceanic biomass eventually solidifies into sedimentary rock. Finally, the atmosphere represents the smallest carbon sink, and the carbon exchange rate to this reservoir is rapid—only about 100 years.

The natural carbon cycle is being disrupted by human activities. Since the dawn of the Industrial Revolution in the late 1700s, people have been burning ever-increasing quantities of **fossil fuels**—deposits of carbon primarily in the form of coal, oil, and natural gas. Fossil fuels contain carbon that was removed from the atmosphere long ago through natural processes and stored in the vast rock reservoir. Normally, this carbon would be re-released back to the atmosphere over millions of years. However, humans are extracting and releasing this material back to the atmosphere in very short periods of time. The atmospheric quantity of CO<sub>2</sub> increased from 270 ppm



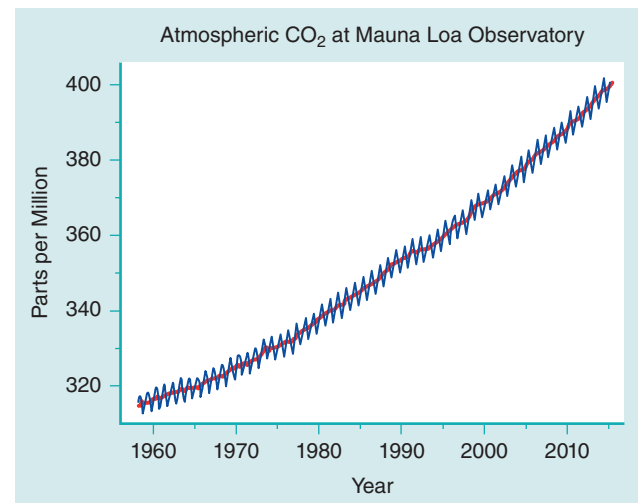
**FIGURE 2.3** Exponential rise in atmospheric carbon dioxide over the past 1000 years.

in 1800 to 407 ppm today, with the bulk of the increase occurring since 1950 (**FIGURE 2.3**).

Whereas clues of the atmospheric concentration of CO<sub>2</sub> in the distant past come from chemical analysis of air bubbles trapped in ice, CO<sub>2</sub> concentration has been measured directly since 1957 atop Mauna Loa in Hawaii—a site as far removed as possible from local sources of pollution. The time series of atmospheric CO<sub>2</sub> since 1957 is known as the **Keeling curve** (**FIGURE 2.4**), named for Charles Keeling, the climatologist who showed that CO<sub>2</sub> released from fossil fuel combustion would accumulate significantly in the atmosphere.

The Keeling curve not only verifies the rapid increase since 1957, but it also reveals the seasonal cycle of CO<sub>2</sub>. Maximum concentrations occur in early spring in the northern hemisphere, where most of the world's middle- and high-latitude forests are located. The relative lack of photosynthetic activity during the dormant northern winter months causes a buildup of atmospheric CO<sub>2</sub> into March. Likewise, minimum atmospheric CO<sub>2</sub> in northern hemisphere autumn results from the buildup of biomass throughout the northern hemisphere's spring and summer months.

The long-term exponential growth in the atmospheric CO<sub>2</sub> concentration concerns most climatologists and environmental scientists. Carbon dioxide is an integral component of Earth's energy balance because it absorbs energy that is radiated from the Earth and then reemits energy back downward to the Earth, thereby keeping the surface warmer than it would be if the CO<sub>2</sub> were not present. This phenomenon is known as the **greenhouse effect**. The rapid increase in the quantity



**FIGURE 2.4** The Keeling curve.

Data from: Scripps Institution of Oceanography and NOAA Earth System Research Laboratory.

of atmospheric CO<sub>2</sub> is considered the culprit for the observed increases in temperature of Earth's surface in the last several decades.

## Constant and Variable Gases

**Constant gases** are those that have relatively long residence times in the atmosphere and that occur in uniform proportions across the globe and upward through the bulk of the atmosphere. These gases include nitrogen, oxygen, argon, neon, helium, krypton, and xenon.

**Variable gases** are those that change in quantity from place to place or over time (**TABLE 2.2**). They generally have shorter residence times than constant gases, as various processes combine to cycle the gases through reservoirs. The most abundant variable gas is water vapor, which can occupy as much as 4% of the lower atmosphere by volume. Higher percentages of water vapor are impossible because atmospheric processes (cloud formation and precipitation) limit the amount that may be present in the atmosphere for any location. The atmosphere is efficient in ridding itself of excess water vapor.

The amount of water vapor in the atmosphere varies widely across space because water and energy must be available at the surface for *evaporation* to occur. Water vapor content is maximized over locations with abundant energy and surface water, so the wettest atmospheres occur over tropical waters and rain forest regions. In addition, water vapor is largely limited to the lower atmosphere because as height increases, atmospheric water vapor is increasingly likely to condense to liquid water in the cooler, high-altitude conditions.

Surprisingly, some locations that experience little precipitation may have abundant water vapor in the atmosphere. The maximum amount of water vapor that may exist in the atmosphere is directly related to air

**TABLE 2.2** Concentrations of Variable Gases of the Atmosphere

Gas	ppm of Air
Water vapor (H <sub>2</sub> O <sub>v</sub> )	0.1–40,000
Carbon dioxide (CO <sub>2</sub> )	~407
Methane (CH <sub>4</sub> )	~1.8
Hydrogen (H <sub>2</sub> )	~0.6
Nitrous oxide (N <sub>2</sub> O)	~0.31
Carbon monoxide (CO)	~0.09
Ozone (O <sub>3</sub> )	~0.4
Fluorocarbon 12 (CCl <sub>2</sub> F <sub>2</sub> )	~0.0005

temperature. When high temperatures combine with a nearby surface water source, high amounts of water vapor are usually present. For example, the Red Sea region tends to have high quantities of atmospheric water vapor despite the lack of precipitation. This region is dry not because water vapor is unavailable but because the region lacks a means by which the precipitation process can occur easily.

As implied by the Red Sea example, deserts are generally not the regions of lowest atmospheric water vapor content. Instead, polar regions are normally the driest locations on Earth. This is because little energy is present in cold air to evaporate water. Furthermore, as air cools, water vapor readily condenses to form clouds and perhaps precipitation, thereby minimizing the mass of water vapor in the atmosphere. So the regions with the least water vapor tend to be the coldest locations on Earth. Over such locations in winter, the water vapor content may approach zero. The total will never actually reach zero because there is always at least some water vapor present in the lower atmosphere, but the total reaches about 0.00001% of the atmospheric volume in central Antarctica.

Several other variable gases are important. Among these, CO<sub>2</sub> is most abundant. As stated earlier, the variable nature of CO<sub>2</sub> stems from its increasing quantity over time, since the late 1700s. The rate of increase is about 0.4% per year or by about 35% since 1800. Other notable variable gases include CH<sub>4</sub>, nitrous oxide (N<sub>2</sub>O), carbon monoxide (CO), tropospheric ozone (O<sub>3</sub>), and a family of chemicals known as **chlorofluorocarbons**

(CFCs). Humans have had at least some influence in the concentration of all these gases, and CFCs are entirely human derived. Collectively, these gases make up only a small amount of the atmosphere, but they can have important implications for some processes.

## ► Faint Young Sun Paradox

Evidence contained in sedimentary rocks and sediments, ice sheets, and fossils reveals that Earth's average temperature has remained within a range of about 15 C° (27 F°) for most, if not all, of its geological history. This implies that even global-scale shifts in mean environmental conditions, from ice ages to ice-free conditions on Earth, have occurred within a range of temperature variability that is smaller than the summer to winter temperature difference at most locations outside the tropics.

This fact has caused considerable consternation for many climate scientists because of an apparent contradiction between what is known about energy released during the evolution of stars, such as our Sun, and evidence of Earth's temperature through geological time. Stars obtain energy through the constant nuclear fusion of hydrogen into heavier elements. These reactions cause stars to expand gradually and grow hotter and brighter over time. Eventually, stars expend their sources of energy and extinguish themselves. We can assume that energy emitted from the early Sun was about 25% to 30% less than that emitted today, because this pattern is observed throughout the life cycle of other stars like the Sun. We also know that even small changes in solar output can induce drastic climatic changes on Earth. If solar output today were decreased by 25% to 30%, temperatures would quickly plummet to a point whereby Earth would be entirely frozen. Because the young Sun must have been weak, at first glance it would appear that Earth must have been frozen for the first 3 billion years of its history. But evidence does not support the notion that Earth was ever below freezing on a global annual average basis. Furthermore, little credible evidence has been found for widespread glaciation during the first half of Earth's existence. This apparent contradiction between a weak Sun but relatively warm global conditions is the **faint young Sun paradox**.

How could temperatures have been above freezing during the early times of geological history? How could Earth maintain a small variance in temperature over time if the Sun were much weaker in the early history of the planet? How could temperatures maintain themselves over time as the Sun grew hotter?

The most logical answer to these questions is that the Earth–ocean–atmosphere system must have some



type of internal regulator that keeps temperatures within a reasonable range regardless of changes to solar output over time. This regulator must have been present in the early atmosphere. How would this have happened? Examining the radiation balance of Earth today reveals that surface temperatures are only indirectly caused by incoming solar radiation—**insolation**—being absorbed at the surface. If surface receipt of solar radiation alone determined temperatures, average Earth temperatures would be about  $-18^{\circ}\text{C}$  ( $0^{\circ}\text{F}$ ). Instead, the transfer of energy (either from the Sun or Earth) absorbed in the atmosphere down to the surface augments radiation received at the surface directly from the Sun. Certain gases in the atmosphere, such as  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , are known to be efficient absorbers of energy escaping the surface. Much of this energy is then reemitted back down to reheat the surface. This process—the greenhouse effect—is responsible for the life-supporting temperatures we enjoy today. The net result is that the average temperature of Earth is raised from  $-18^{\circ}\text{C}$  ( $0^{\circ}\text{F}$ ) to a more comfortable  $15^{\circ}\text{C}$  ( $59^{\circ}\text{F}$ ).

So which **greenhouse gases** could have helped the early Earth to remain relatively warm? The two most abundant greenhouse gases in today's atmosphere are water vapor and  $\text{CO}_2$ . As far as we can tell, the quantity of water vapor has remained relatively constant since primordial times. Until recently it was assumed that the wide fluctuations of  $\text{CO}_2$  over time caused Earth's temperature to remain relatively stable via the greenhouse effect. That argument suggests that during times in Earth history when the Sun was relatively weak, such as in Earth's early atmosphere, the high concentrations of  $\text{CO}_2$  may have effectively absorbed large amounts of radiation emitted from Earth and reemitted much of that radiation back downward in the greenhouse effect. Just as the solar output began to increase, the onset of plant evolution and proliferation would have been removing enough atmospheric  $\text{CO}_2$  to keep the insolation and temperatures on Earth fairly constant.

But if excessive levels of  $\text{CO}_2$  indeed caused Earth to remain warm despite a weak Sun, such concentrations probably would have been too high to allow the generation of organic molecules, so life could not have existed easily. Furthermore, no geological evidence has been found to suggest that  $\text{CO}_2$  concentrations were ever large enough to have created such a strong greenhouse effect. Specifically, in an oxygen-free atmosphere such as early Earth would have had,  $\text{CO}_2$  levels of about eight times today's concentrations would have produced the mineral **siderite** ( $\text{FeCO}_3$ ) in the top layers of the soil as iron reacted with the  $\text{CO}_2$ , but not enough  $\text{FeCO}_3$  has been found in relic soils to support this hypothesis. Better explanations for the faint young Sun paradox were sought.

A second explanation is that ammonia ( $\text{NH}_3$ ) caused the early greenhouse effect. This hypothesis was proposed by Carl Sagan and George Mullen of Cornell University in the late 1970s and was based on the observation that  $\text{NH}_3$  behaves as a strong greenhouse gas. The problem with this argument is that experiments have shown that  $\text{NH}_3$  is easily broken up by UV radiation in oxygen-free conditions, such as in the atmosphere before the arrival of photosynthesis. Nevertheless, the  $\text{NH}_3$  explanation is still plausible because shielding by other gases may have allowed  $\text{NH}_3$  to accumulate in the lower atmosphere and be an important greenhouse gas.

A third explanation, proposed by Harvard scientists in the early 2000s, is that in the pre-photosynthesis Earth, the planet's oxygen-devoid atmosphere made conditions ideal for oxygen-intolerant microbes called **methanogens**. These methanogens (so-named because they release  $\text{CH}_4$  as a waste product) likely allowed  $\text{CH}_4$  to produce a strong greenhouse effect, which would have warmed Earth even though the Sun emitted less radiation at the time. It is well known that  $\text{CH}_4$  is a highly effective greenhouse gas. Once oxygen entered the atmosphere from photosynthesis, the methanogens began to die off and  $\text{CH}_4$  became less important as a greenhouse gas. In today's oxygen-rich atmosphere the concentration of  $\text{CH}_4$  is extremely minute—an average of only 1.8 ppm in the atmosphere. Some geoscientists surmise that the demise of the methanogens caused Earth's first global ice age and perhaps contributed to subsequent ice ages.

Regardless of the explanation, most of Earth's history is thought to have been dominated by somewhat higher temperatures than exist today, or at least temperatures that are not far below those now. The debate over the explanation of the faint young Sun paradox lingers on.

## ► Atmospheric Structure

The atmosphere may be divided into a series of layers based on thermal qualities (**FIGURE 2.5**). The lowest layer of the atmosphere is called the **troposphere**. This is a very thin zone confined to the first 8 to 20 km (5 to 12 mi) above Earth's surface, yet this atmospheric layer contains approximately 75% of the mass of the atmosphere. The compressibility of air allows its weight to exert a downward force on, and compress, the lower atmosphere. This layer therefore also contains air of the greatest mass per unit volume: **density**.

The term "troposphere" is derived from the Greek word meaning "to turn." This indicates that the troposphere is a region in which mass is constantly overturning, largely as a result of thermodynamic (heat-driven) processes. Most insolation passes through the atmosphere

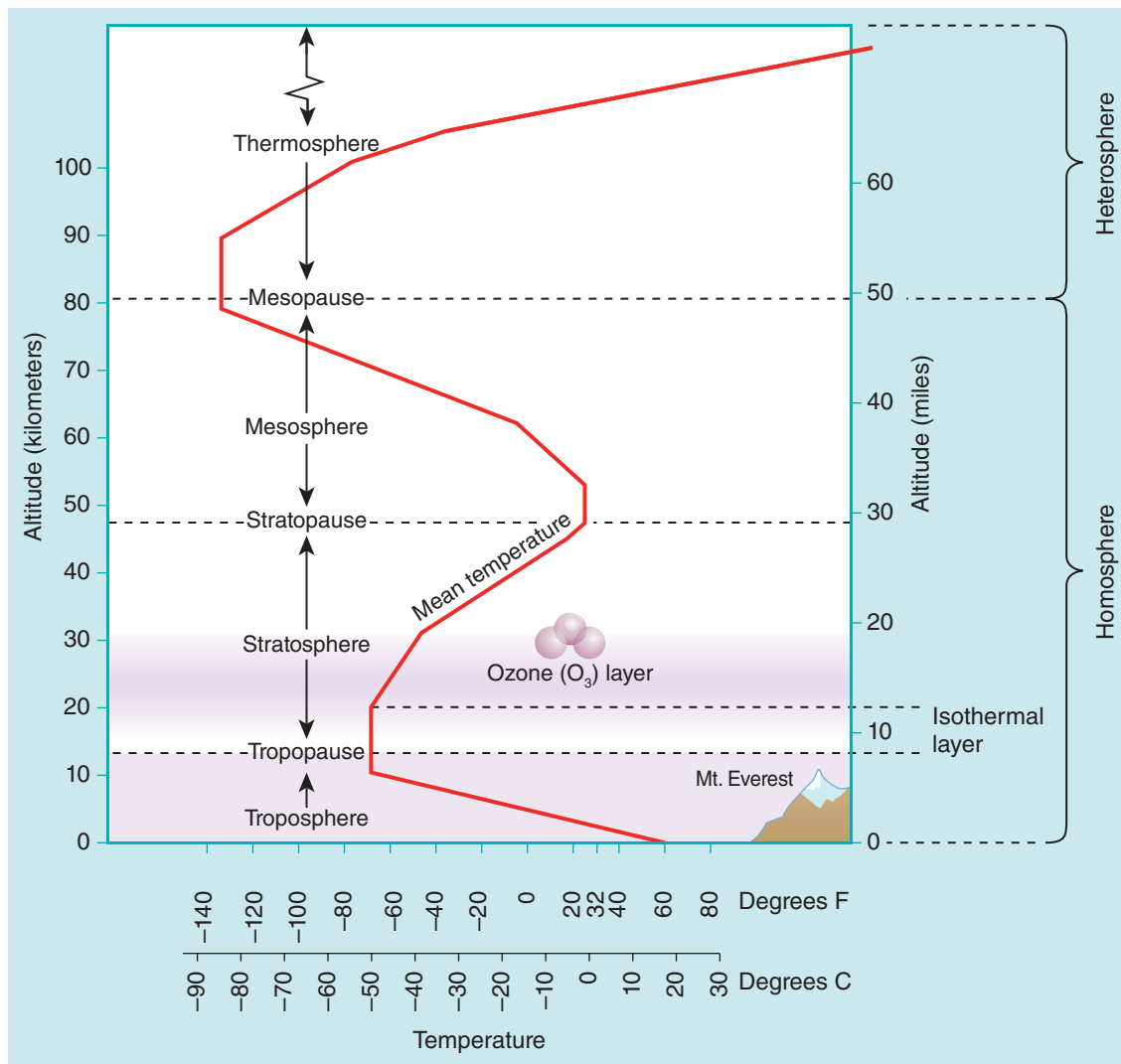


FIGURE 2.5 The vertical structure of the atmosphere.

before being absorbed by the Earth's surface. The heated surface then warms the air directly above it through the process of **conduction**. This gives the lowest layers of the atmosphere buoyancy and causes the air to rise in a process known as **convection**. Eventually this air cools and sinks. Because this vertical movement is integral to the development of most weather-related processes, the troposphere is sometimes referred to as the "weather sphere."

Because the atmosphere is heated primarily from Earth's surface and because the compression of atmospheric gas decreases with height (as the weight of the atmosphere above it decreases), a decrease of temperature usually occurs with increasing height through the troposphere. This decrease is known as the **environmental lapse rate**. Through the troposphere, air cools at an average rate of  $6.5\text{ }^{\circ}\text{C}/\text{km}$  (or  $3.5\text{ }^{\circ}\text{F}/1000\text{ ft}$ ), although this value may vary widely from place to place and from day to day, and even on an hourly basis.

According to one form of **Charles' law**, in an ideal gas (which the atmosphere approximates), density decreases as temperature increases if pressure remains constant. Air that is warmer than surrounding air thus rises. Because Earth is not heated equally and relatively warm air rises, the troposphere does not have a uniform depth. Instead, the troposphere is thicker near the equator than near the poles. Near the equator the layer is approximately 20 km (12 mi) thick, whereas near the poles in winter the thickness is only about 8 km (5 mi). Roughly the same amount of atmospheric mass exists over the two locations, but the density of that air is less over the equator and greater over the poles.

The top of the troposphere is called the **tropopause**. This feature marks the boundary between the troposphere below and the next layer of the atmosphere above (Figure 2.5). The average temperature at the tropopause is about  $-57^{\circ}\text{C}$  ( $-70^{\circ}\text{F}$ ), which represents quite

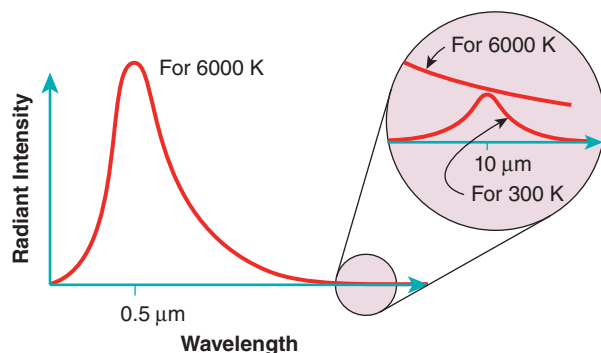


a decrease from the 15°C (59°F) average temperature of the surface.

The layer above the troposphere is the **stratosphere**. Temperatures remain somewhat constant from the tropopause upward into the stratosphere for about 10 km (6 mi). Any zone of relatively constant temperature with height, such as this one, is called an **isothermal layer**. Above the isothermal layer temperatures actually increase with height through the rest of the stratosphere. This increase of temperature with height—a **temperature inversion**—is caused by the absorption of UV radiation by the triatomic form of oxygen ( $O_3$ ), or ozone.

The so-called ozone layer in the stratosphere occurs because of several processes that have important implications for terrestrial life on the planet. To understand the workings of the ozone layer we must first review the nature of radiation reaching Earth from the Sun. Insolation arrives in Earth's atmosphere in a wide range of **wavelengths**, which are measured in **micrometers** (millionths of a meter [ $\mu\text{m}$ ]). Shorter wavelengths are associated with more intense (and therefore more harmful to living things) energy than longer wavelengths. The Sun emits more energy at a wavelength of about 0.5  $\mu\text{m}$  than at any other wavelength, with successively less energy emitted at successively shorter and longer wavelengths (**FIGURE 2.6**). By convention, energy from solar origin shorter than 4.0  $\mu\text{m}$  is usually referred to as **shortwave radiation** in the atmospheric sciences. Wavelengths of the peak amounts of shortwave radiation occur in the visible part (0.4 to 0.7  $\mu\text{m}$ ) of the **electromagnetic spectrum**—the full assemblage of all possible wavelengths of electromagnetic energy.

Any insolation with wavelengths less than 0.4  $\mu\text{m}$  is too intense to allow terrestrial life to exist. UV radiation falls between wavelengths of 0.01 and 0.40  $\mu\text{m}$ , making UV radiation harmful to living organisms. Fortunately,  $N_2$  absorbs electromagnetic radiation of wavelengths below 0.12  $\mu\text{m}$ . But how does the ozone layer protect us from UV radiation at wavelengths between 0.12 and 0.40  $\mu\text{m}$ ?



**FIGURE 2.6** Emitted energy by wavelength for the Sun and Earth, assuming a surface temperature of 6000 K for the Sun and 300 K for the Earth.

Some of the diatomic oxygen ( $O_2$ ) that enters the atmosphere from photosynthesis near the surface reaches the stratosphere over time. Because  $O_2$  molecules effectively absorb UV radiation at wavelengths between 0.12 and 0.18  $\mu\text{m}$ , the  $O_2$  reaching the stratosphere is exposed to incoming harmful radiation. When this radiant energy strikes  $O_2$  molecules, a chemical reaction in the presence of light that splits the molecular bonds—**photodissociation**—is triggered and two monatomic oxygen (O) atoms are liberated. Because O is inherently unstable, it bonds quickly and easily with other atoms and molecules. Some of these O atoms chemically bond with an  $O_2$  molecule to form an  $O_3$  molecule that effectively absorbs UV radiation at wavelengths between 0.18 and 0.34  $\mu\text{m}$ . But in the absorption process the  $O_3$  becomes photodissociated into O and  $O_2$ , and the O then bonds with another  $O_2$  to form  $O_3$ . The process then repeats endlessly, ensuring that oxygen is continuously being reworked into  $O_3$  in the stratosphere. UV radiation at wavelengths between 0.18 and 0.34  $\mu\text{m}$  is effectively “absorbed”—actually used in chemical processes with emitted heat as a byproduct—such that only the UV radiation at wavelengths between 0.34 and 0.40  $\mu\text{m}$  filters to Earth's surface. This harmful radiation can cause skin cancer, cataracts, and other problems if we are exposed to it in large doses, but at least we are protected from the much more harmful shorter UV wavelengths.

Early in geological history, the first organisms must have formed in murky waters because no  $O_2$  (and, therefore, no  $O_3$ ) existed to protect them from UV radiation. By the time life evolved into shallow water areas and onto land surfaces,  $O_2$  released from photosynthesis had built a stratospheric  $O_3$  layer. Life has never been exposed to excessive amounts of UV radiation and has never adapted to it. Increasing exposure to UV radiation is damaging to terrestrial life.

Humans have contributed to thinning the fragile  $O_3$  layer over the past half-century by producing CFCs. Most general uses for CFCs involved refrigeration both as a gas (Freon) and as an insulating substance (foam and Styrofoam). CFCs were also used as a propellant for aerosol sprays. When chlorine from CFCs and bromine are released to the atmosphere, they can make their way upward to the stratosphere where they readily bond with monatomic oxygen atoms. Such a bond does not allow the O to bond with  $O_2$  to produce the  $O_3$  that would absorb UV radiation. The result is that increased amounts of UV radiation reach the surface, where adverse effects on organisms occur. Although  $O_3$  is found throughout the stratosphere, if all stratospheric ozone were compressed to the surface it would create a layer only 3 mm thick. Since the U.S. ban on CFC production took effect on January 1, 1996, the ozone layer has shown some signs of recovery.

The ozone formation process is responsible for the temperature inversion in the stratosphere. As  $O_3$  molecules absorb UV radiation, they acquire energy. The  $O_3$  at the top of the stratosphere has the first opportunity to gain energy (and, therefore, temperature, because temperature is a measure of the energy or heat content of matter) from incoming UV radiation. Its temperature, therefore, is higher than for molecules lower in the stratosphere. The process of  $O_3$  production and dissociation happens in the stratosphere because this is the uppermost layer for which atmospheric density is high enough to allow O and  $O_2$  to meet and bond quickly enough so that incoming UV radiation is absorbed effectively. Temperatures rise to approximately  $-18^\circ\text{C}$  ( $0^\circ\text{F}$ ) at the **stratopause**, which is about 48 km (29 mi) above the surface. The stratopause is the boundary between the stratosphere and the layer above it.

The layer above the stratosphere is the **mesosphere**, from the Greek prefix *meso-*, which means “middle.” Although this layer does sit near the middle of the atmosphere from an altitude perspective—in the region between the stratopause and about 80 km (50 mi) above the surface—the low-density mesosphere does not represent the middle of the atmosphere by density or volume. Because of the compressibility of gases, the middle of the atmosphere by density and volume is only about 5.5 km (3.4 mi) above the surface—well within the troposphere.

Similar to the troposphere, temperatures in the mesosphere decrease with height. The temperature inversion characteristic of the stratosphere is not present in the mesosphere because it is too high for photodissociated  $O_2$  to encounter other oxygen atoms or molecules to bond with quickly enough to absorb the incoming UV radiation. Instead, the increased density and proximity to the surface and stratospheric heat sources below the mesosphere make the lower mesosphere warmer than the top of this layer. Temperatures at the **mesopause** average approximately  $-84^\circ\text{C}$  ( $-120^\circ\text{F}$ ).

Few processes of consequence to weather and climate are known to occur in the mesosphere in part because so little atmospheric mass exists in this zone. Charged particles from the Sun that are captured by Earth’s magnetic field in the mesosphere can disrupt telecommunications during their release of energy. These same charged particles are also responsible for the northern lights (*aurora borealis*; **FIGURE 2.7**) and southern lights (*aurora australis*). But even these processes have minimal effect on Earth’s weather and climate.

From the surface up through the mesosphere, the proportion of atmospheric gases is about the same as that at the surface, except for the greater concentration of  $O_3$  in the stratosphere. The first three “spheres” of the atmosphere are thus sometimes collectively known as the **homosphere**, which means “same sphere.” Above



**FIGURE 2.7** The *aurora borealis*.

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the mesosphere gases stratify into layers according to their atomic weights because there is so little mass to “stir them up.” That region is termed the **heterosphere**.

The heterosphere corresponds to the final thermal layer of the atmosphere, the **thermosphere**. Like the stratosphere, the thermosphere is characterized by temperatures that increase with height—a temperature inversion. Unlike the stratosphere, however, where the inversion exists because of O<sub>3</sub> absorption of insolation, the thermospheric temperature inversion occurs because the uppermost N<sub>2</sub> and O<sub>2</sub> molecules have the first opportunity to absorb insolation. Their position allows them to attain extraordinarily high temperatures because Earth’s magnetic field captures charged high-energy particles from the Sun.

The number of those molecules with such high temperatures is miniscule, however, because of the sparseness of the atmosphere at such heights. The total mass of the thermosphere accounts for only about 0.01% of the total atmospheric mass. The decrease of density, mass, and volume of the atmosphere can be expressed by the **mean free path** of a molecule—the distance an individual molecule must travel before encountering another molecule. The mean free path at the surface is on the order of a micrometer. By contrast, in the thermosphere the mean free path is on the order of a kilometer or more. Despite the fact that the individual molecules have very high amounts of energy, there are so few molecules to contain the heat that even if you could somehow survive for more than a fraction of a second at those heights, you would freeze to death instantly even at temperatures above 1100°C (2000°F)!

A thermopause does not exist; instead, the atmosphere simply merges slowly into interplanetary space. Individual gas molecules may be gravitationally attracted to the planet for quite a distance into space. Most agree, however, that the atmosphere extends no higher than about 1000 km (600 mi) above the Earth’s surface.

## ► Summary

The atmosphere is a fragile and complex collection of gases gravitationally attracted to Earth. It originated early in the history of the planet as volcanic materials cooled and outgassed. The early atmosphere is believed to have been composed primarily of N<sub>2</sub> and CO<sub>2</sub>, but O<sub>2</sub> gradually replaced CO<sub>2</sub> as the second-most abundant gas since the evolution and proliferation of simple organisms and green plants, which have stored carbon in their biomass and released O<sub>2</sub> into the atmosphere over the past 3 billion years.

Carbon is stored for certain periods of time within a number of reservoirs such as rock layers, the ocean, biomass, and the atmosphere. This cycle of carbon is important in the history of Earth. Its importance has been challenged recently, however, by evidence suggesting that methane-emitting microbes may have played a greater role than previously believed in Earth’s early history by absorbing energy emitted by Earth via the greenhouse effect. This methane may have kept Earth’s temperatures within a narrow range of variability, despite a weaker solar output.

The troposphere is the lowest layer of the atmosphere and is where nearly all weather and climate processes of importance occur. Temperatures in the troposphere usually decrease with height because of the increased density in the most compressed part of the atmosphere—the part nearest to the surface—and because of proximity to the surface, which absorbs insolation more effectively than the air above it. The stratosphere is the second layer from the surface and is characterized by increases in temperature with height—a temperature inversion—because of ozone absorption. In the mesosphere temperatures decrease with height for the same reason they do in the troposphere. The final thermal layer of the atmosphere is the thermosphere, which is characterized by a temperature inversion because of the direct absorption of incoming radiation by N<sub>2</sub> and O<sub>2</sub>.

## Key Terms

Aerosol

*Atmosphere*

*Biosphere*

Carbon cycle

Charles’ law

Chlorofluorocarbon (CFC)

Condensation

Conduction

Constant gas

Convection

Density

Diffusion

Electromagnetic spectrum

Environmental lapse rate

Eukaryote

*Evaporation*

Faint young Sun paradox

Fermentation

Flux

Fossil fuel

Greenhouse effect

Greenhouse gas

Heterosphere

Homosphere

*Hydrosphere*

Hydrostatic equilibrium

Insolation

Isothermal layer

Keeling curve

*Lithosphere*

Mean free path	Ozone (O <sub>3</sub> )	Sink
Mesopause	Photodissociation	Solar wind
Mesosphere	Photosynthesis	Stratopause
Methane (CH <sub>4</sub> )	Planetesimal	Stratosphere
Methanogen	Prokaryote	Temperature inversion
Micrometer	Reservoir	Thermosphere
Nebula	Residence time	Tropopause
Newton's second law of motion	Respiration	Troposphere
Nuclear fusion	Second law of thermodynamics	Ultraviolet (UV) radiation
Oort cloud	Shortwave radiation	Variable gas
Outgassing	Siderite	Wavelength

*Terms in italics also appeared in Chapter 1.*

## Review Questions

1. Explain how Earth and its atmosphere formed.
2. How is today's atmosphere similar to and different from early Earth's atmosphere?
3. Describe how oxygen came to comprise almost 21% of the atmosphere today.
4. Given that solar output has increased over the past 4.6 billion years, how have Earth's temperatures remained fairly constant over that same time?
5. What is residence time and why is it important?
6. What is the carbon cycle and how does it operate?
7. Describe the thermal structure of the atmosphere.
8. What causes the thermal characteristics associated with each thermal layer of the atmosphere?
9. Compare and contrast the heterosphere and the homosphere.
10. Why is there no defined top to the atmosphere?

## Questions for Thought

1. Give as many examples of the second law of thermodynamics as you can think of, both related to and not related to the atmosphere.
2. Why do the *aurora borealis* and *aurora australis* occur in the mesosphere and not elsewhere in the atmosphere?
3. Why are the auroras not visible in the tropical parts of the Earth?