CHAPTER ONE

The Big Questions

1.1 OVERVIEW

This chapter will survey a few of the major questions raised by observed features of present and past Earth and planetary climates. Some of these questions have been answered to one extent or another, but many remain largely unresolved. This will not be a comprehensive synopsis of Earth and planetary climate evolution; we will be content to point out a few striking facts about climate that demand a physical explanation. Then, in subsequent chapters, we'll develop the physics necessary to think about these problems. Although we hope not to be too Earth-centric in this book, in the present chapter we will perforce talk at greater length about Earth's climate than about those of other planets, because so much more is known about Earth's past climate than is known about the past climates of other planets. A careful study of Earth history suggests generalities that may apply to other planets, and also raises interesting questions about how things might have happened differently elsewhere, and it is with this goal in mind that we begin our journey.

1.2 CLOSE TO HOME

When the young Carl Linnaeus set off on his journey of botanical discovery to Lapland in 1732, he left on foot from his home in Uppsala. He didn't wait until he reached his destination to start making observations, but found interesting things to think about all along the way, even in the plant life at his doorstep. So it is with climate as well.

To the discerning and sufficiently curious observer, a glance out the window, a walk through the woods or town, a short sail on the ocean, all raise profound questions about the physics of climate. Even without a thermometer, we have a perception of "heat" or "temperature" by examining the physical and chemical transitions of the matter around us. In the summertime, ice cream will melt when left out in the sun, but steel cooking pots don't. Trees and grass do not spontaneously burst into flame every afternoon, and a glass of water left outdoors in the summer does not boil. Away from the tropical regions, it often gets cold enough for water to freeze in the wintertime, but hardly ever cold enough for alcohol to freeze. What is it that heats the Earth? Is it really the Sun, as seems intuitive from the perception of warmth on a sunny day? In that case, what keeps the Earth from just accumulating more and more energy from the Sun each day, heating up until it melts? For that matter, why don't temperatures plummet to frigid wintry values every night when the Sun goes down? Similarly, what limits how cold it gets during the winter?

With the aid of a thermometer, such questions can be expressed quantitatively. The first, and still most familiar, kinds of thermometers were based on one particular reproducible and measurable effect of temperature on matter – the expansion of matter as it heats up. Because living things are composed largely of liquid water, the states of water provide a natural reference on which to build a temperature scale. The *Celsius* temperature scale divides the range of temperature between the freezing point of pure water and the boiling point at sea level into 100 equal steps, with zero being at the freezing point and 100°C at the boiling point.[1]

Through observations of fire and forge, even the ancients were aware that conditions could be much hotter than the range of temperatures experienced in the normal course of climate. However, they could have had no real awareness of how much *colder* things could get. That had to await the theoretical insights provided by the development of thermodynamics in the nineteenth century, followed by the invention of refrigeration by Carl von Linde not long afterwards. By the close of the century, temperatures low enough to liquify air had been achieved. This was still not as low as temperatures could go. The theoretical and experimental developments of the nineteenth century consolidated earlier speculations that there is an *absolute zero* of temperature, at which random molecular motions cease and the volume of an ideal gas would collapse to zero; no temperature could go below this absolute zero. On the Celsius scale, absolute zero occurs at −273.15 °C. Most of thermodynamics and radiation physics can be expressed more cleanly if temperatures are given relative to absolute zero, which led to the formulation of the *Kelvin* temperature scale, which shifts the zero of the scale while keeping the size of the units the same as on the Celsius scale. On the Kelvin scale, absolute zero is at zero kelvin, the freezing point of water is at 273.15 K, and the sea-level boiling point of water is at 373.15 K. Viewed on the Kelvin scale, the temperature range of Earth's climate seems quite impressively narrow. It amounts to approximately a ±10% variation about a typical temperature of 285 K. A 20% variation in the Earth's temperature (as viewed on the Kelvin scale) would be quite catastrophic for life as we know it. This remark can be encapsulated in a saying: "Physics may work in degrees Kelvin, but Earth life works in degrees Celsius."

There is more to climate than temperature. Climate is also characterized by the amount and distribution of precipitation (rainfall and snowfall), as well as patterns of atmospheric winds and oceanic currents. However, temperature will do for starters. In this book we will discuss temperature at considerable length, and venture to a somewhat lesser degree into the factors governing the amount of precipitation. We will not say much about wind

[1] The scale is named for the Swedish astronomer Anders Celsius, who originally formulated a similar temperature scale in 1742. Celsius' scale was reversed relative to the modern one, putting 100 at the freezing point and zero at the boiling point. The Celsius scale is sometimes called *centigrade*, but Celsius is considered to be the preferred term. The official definition of the temperature scale is now based on standards that are more precise and unambiguous than the freezing and boiling points of water.

patterns, though some of their effects on the temperature distribution will be discussed in Chapter 9.

If you live outside the tropical zone, you will come to wonder why it is hotter in summer than in winter, and why the summer/winter temperature range has the value that it does (e.g. 30 °C in Chicago) and why the variation is generally lower over the oceans (e.g. 7 °C in the middle of the Pacific Ocean, at the same latitude as Chicago). If you communicate with friends living in the Arctic or Antarctic regions, and other friends living near the Equator, you will begin to wonder why, on average, it is warmer near the Equator than in the polar regions, and why the temperature difference has the value it does (e.g. 40 °C difference between the annual average around the Equator and the annual average at the north pole). The physics underlying the seasonal cycle and the pole to Equator temperature gradient is discussed in Chapters 7 and 9. If you climb a mountain (or even observe the snow-capped peaks of a mountain from the valley floor on a hot summer day), or if you go up in a hot-air balloon, or fly in an airliner which informs you of the outdoor temperature – you will notice that the air gets colder as one goes higher in altitude. Why should this be? This turns out to be a general feature of planetary atmospheres, and the basic physics underlying the phenomenon is discussed in Chapter 2.

The air that surrounds us is itself a matter of interest. We know that it is there because it has a temperature and exerts pressure, and because it is necessary that we breathe it in order to remain alive. But what is the air made of, and why does it have the composition it does? We can see water condense out of the air, but why don't other components condense in the course of natural weather and climate variations? How much air is there? And has it always been there with its present composition, or has it changed over time? If so, how much and how quickly?

We know that our planet journeys through the hard vacuum of outer space, clothed in a thin blanket of air – our atmosphere. It is natural to wonder how our atmosphere affects the Earth's climate. The airless Moon shares the orbit of the Earth, at the same distance from the Sun, so one can look to the Moon to get an idea of what the Earth's climate would be like if it had no atmosphere. We know the Moon is airless because a reasonably thick atmosphere would bend the light rays from the Sun and stars, just as objects appear displaced when viewed through the surface of a swimming pool. But how to measure its temperature?

Of course, one could go there with a thermometer (and this did eventually happen) but people became curious about lunar conditions long before it seemed likely that anybody would ever get there. Dante Alighieri himself, in the *Paradiso* written between 1308 and 1321, devoted fully one hundred cantos to a learned discussion between himself and Beatrice concerning the source of lunar light and the solidity of the lunar surface. By the mid nineteenth century, science had progressed to the point that the questions could be formulated more sharply, and the means for an answer had begun to emerge. With the discovery of infrared light by Sir William Herschel in 1800, astronomy opened a new window into the properties of planets and stars. Over the coming decades, it gradually became clear that all bodies emit radiation according to their temperature. This is known as *blackbody radiation* and will be discussed in detail in Chapter 3. Infrared light from the Moon was detected by Charles Piazzi Smyth in 1856, and the first attempt to use it to estimate temperature was by the Fourth Earl of Rosse in 1870. The instruments available at the time were not up to the task. In 1878, Langley invented the bolometer, which made good observations of lunar infrared radiation possible. However, while Langley made the first accurate observations of lunar infrared, theory was not quite up to the task of interpreting the observations. These issues were largely sorted out by 1913, though Langley gave up on his earlier estimates

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rather reluctantly. By 1913 it was pretty clear that the daytime temperature of the Moon at the point where the Sun is directly overhead is well in excess of 373 K (the sea-level temperature of boiling water on Earth). Night-time temperatures were harder to determine accurately, since the infrared emission from cold objects is weak; however, it was clear that temperatures at night dropped by well over 140 K relative to the daytime peak. Pettit and Nicholson observed the temperature of the Moon during the lunar eclipse of 1927, using the Mt. Wilson telescope. They found something even more remarkable: over the span of the few hours of the eclipse, the lunar temperature fell from 342 K at the point of observation to 175 K. Modern measurements show the daily average temperature at the lunar equator to be around 220 K, while the mean temperature at 85° N latitude is 130 K.

It appears that without an atmosphere or ocean, the Earth would be subject to extreme swings of temperature between day and night. The Moon's "day" is 28 Earth days, since it always shows the same face to the Earth; on that basis, one could imagine that the day/night extremes were due to a longer night offering more time to cool down, but the rapid cooling during an eclipse gives the lie to this idea. Given the rapid cooling of an airless body at night, it is likely that the Earth's summer/winter temperature difference would be far more extreme in the absence of an atmosphere. Further, a comparison of the pole to equator gradient in daily mean temperature with that on Earth suggests that the atmosphere significantly moderates this gradient, too. What is it about the atmosphere or ocean that damps down day/night or summer/winter swings in temperature? This subject will be taken up in Chapter 7, where we'll also learn why summer is warmer than winter and why the poles are on the average colder than the equator. How does an atmosphere or ocean moderate the temperature difference between pole and equator? We'll learn something of that in Chapter 9.

At its hottest the Moon gets much hotter than Earth, and at its coldest it gets much colder. But how does the Moon's mean temperature stack up against that of Earth? The 220 K mean equatorial temperature of the Moon is very much colder than the observed mean tropical temperature on Earth, which is on the order of 300 K. If the Earth's mean temperature were as low as that of the Moon, the oceans would be solidly frozen over. The cold mean temperature of the Moon does not come about because the Moon reflects more sunlight than the Earth; the Moon looks silvery but measurements show that it actually reflects less than Earth. Why is the Earth, on average, so much warmer than the Moon? Does this have something to do with our atmosphere, or is it the case that Earth is warmed by some internal heat source that the Moon lacks?

The search for the first stirrings of an answer to this problem takes us back to 1827, when Fourier published his seminal treatise on the temperature of the Earth. Fourier could not have known anything about the temperature of the Moon, but he did know a great deal about heat transfer – having in fact largely invented the subject. Using his new theory of heat conduction in solids, Fourier analyzed data on the rate at which average temperature increases as one descends deeper below the Earth's surface; he also analyzed the attenuation of day/night or summer/winter temperature fluctuations with depth. (Fourier's solution for the latter problem will be derived in Chapter 7.) Based on these analyses, Fourier concluded that the flow of heat outward from the interior of the Earth was utterly insignificant in comparison to the heat received from the Sun. We will see shortly that this situation applies to other rocky planets as well: dry rock is a good insulator, and doesn't let internal heat out very easily.

If the Earth is continually absorbing solar energy, it must also have some way of getting rid of it. Otherwise the energy would have accumulated over the past eons, leading to a molten, incandescent uninhabitable planet (see Problem 3.2) – which is manifestly not the case. Fourier seems to have known that there was little or no matter in the space through which planets plied their orbits, and so he posited that planets lose heat almost exclusively through emission of infrared radiation (called "dark heat" at the time).[2] He also knew that the rate of emission of "dark heat" increased with temperature, which provided a means for an equilibrium temperature to be achieved: a planet would simply heat up until it radiated infrared energy at the same rate as it received energy from the Sun. Finally, Fourier refers to experiments showing that something in the atmosphere emits infrared radiation downward toward the ground, and seems to have been aware also of the fact that something in the atmosphere absorbs infrared. Based on these somewhat sketchy observations, Fourier inferred that the Earth's atmosphere retards the emission of infrared to space, allowing it to be warmer than it would be if it were airless.

Fourier's treatise made it clear that the thermal emission of infrared light was not just useful for astronomical observations – it was in fact part and parcel of the operation of planetary climate. At Fourier's time the state of understanding of infrared radiation emission was not sufficiently developed to allow him to complete the calculation he set up. Nonetheless, he correctly formulated the problem of terrestrial temperature as one of achieving a balance between the rate at which solar radiation is absorbed and the rate at which infrared is emitted. With this great insight, the modern era of study of planetary temperature had begun. Fleshing out the "details," however, required major advances in several areas of fundamental physics. The basic principles of planetary energy balance, and of the manner in which an atmosphere increases planetary temperature, are introduced in Chapter 3 and elaborated on in the earlier parts of Chapter 4.

One of the many details that needed to be settled was the question of which components of the atmosphere affected the transmission of infrared radiation. In 1859 Tyndall found that the dominant components of the Earth's atmosphere – nitrogen (in the form of N_2) and oxygen (in the form of O_2) – are very nearly transparent to infrared radiation. He found instead that it was two relatively minor constituents – water vapor and CO_2 – which accounted for most of the infrared absorption and emission by Earth's air. Gases of this sort, which let solar energy through virtually unimpeded but strongly retard the outward loss of infrared radiation, are known as *greenhouse gases*. Their warming effect on the lower portions of a planet's atmosphere, and on its surface (if it has one), is called the "greenhouse effect." The term was not coined by Fourier, and in some ways is misleading, since real greenhouses do not work by blocking infrared emission. However, the glass or plastic enclosure of a real greenhouse does warm the interior by reducing heat loss to the environment while allowing solar heating, and in that sense – viewed as a broader metaphor for the implications of energy balance – the analogy is apt. Besides CO_2 and water vapor, we now know of a number of additional greenhouse gases, including CH_4 (methane), which may have played a very important role on the Early Earth, and plays some role even today. In fact, it turns out that in some very dense atmospheres such as that of Titan, even nitrogen can become a greenhouse gas. What determines whether a molecule is or is not a good greenhouse gas, and how do we characterize the effects of individual gases, and thus the

[2] Fourier also refers to the importance of heating from what he calls the "temperature of space." It is unclear whether he thought there was some substance in space that could conduct heat to the atmosphere, or whether he was referring to some invisible radiation which pervades space. His inferences regarding the importance of this factor were erroneous – the only real error in an otherwise remarkable paper.

influence of atmospheric composition on climate? These questions will be taken up in the latter half of Chapter 4.

In thinking about the effect of greenhouse gases on climate, it is important to distinguish between *long-lived greenhouse gases* which are removed slowly from the atmosphere on a time scale of thousands of years or more, and *short-lived greenhouse gases* which are removed on a time scale of weeks to years by condensation or rapid chemical reactions. The short-lived greenhouse gases act primarily as a feedback mechanism. Their concentration adjusts rapidly to other changes in the climate, serving to amplify or offset climate changes caused by other factors – including changes due to long-lived greenhouse gases. Long-lived greenhouse gases can also participate in feedbacks, but only on time scales longer than their typical atmospheric adjustment time. Whether a greenhouse gas is long-lived or short-lived depends on environmental conditions. On the Earth, CO_2 is a long-lived greenhouse gas but water vapor is a short-lived greenhouse gas; however, on Mars, which gets cold enough for CO_2 to condense, that gas can be considered short-lived.

Greenhouse gases are largely invisible, but the atmosphere also holds a readily visible component that exerts a profound influence over our planet's energy balance – the clouds. Clouds on Earth are composed of suspended droplets of condensed water, in the form of liquid or ice. Clouds, like water vapor, act as a short-lived greenhouse gas affecting the rate at which infrared can escape to space. The infrared opacity of clouds is used routinely in weather satellites, since this property makes cloud patterns visible from space even on the night side of the Earth. However, clouds affect the other side of the energy balance as well, because cloud particles quite effectively reflect sunlight back to space. The two competing effects of clouds are individually large, but partly offset each other, so that small errors in one or the other term lead to large errors in the net effect of clouds on climate. Moreover, the effect of clouds on the energy budget depends on all the intricacies of the physics that determine things like particle size and how much condensed water remains in suspension. For this reason, clouds pose a very severe challenge to the understanding of climate. This is the case not just for Earth, but for virtually any planet with an atmosphere. The physics underlying the effects of clouds on both sides of the radiation balance will be discussed in Chapters 4 and 5.

1.3 INTO DEEPEST TIME: FAINT YOUNG SUN AND HABITABILITY OF THE EARTH

The Solar System was not always as we see it today. It formed from a nebula of material collapsing under the influence of its own gravitation, and once the nebula began to collapse, things happened very quickly. The initial stage of formation of the Solar System was complete by about 4.6 billion years ago. By this time, the Sun had begun producing energy by thermonuclear fusion; the formation of the outer gas giant planets and their icy moons by condensation, and the formation of the inner planets by collision of smaller rocky planetesimals, were essentially complete. The last major event in the formation of the Earth was collision with a Mars-sized body 4.5 billion years ago, which formed the Moon and may have melted the Earth's primitive crust in the process. All these collisions left behind a great deal of heat that had to be gotten rid of before the crust could stabilize. To determine how long it takes to get rid of this heat, we must learn about the mechanisms by which planets lose energy, and about how the rate of energy loss depends on temperature and atmospheric composition; this will happen in Chapters 3 and 4. It turns out that a planet loses energy almost exclusively by radiation of infrared light to space. While the precise rate of loss depends on the nature of the atmosphere, all estimates show that the surface of the Earth quickly cools to 2000 K, at which point molten rock solidifies; in the absence of an atmosphere, this process takes a thousand years or less, while with a thick atmosphere it could take as long as two or three million years.

Once a solid crust forms, the flow of heat from the interior of the Earth to the surface is sharply curtailed, because heat diffuses very slowly through solid rock. In this situation, supply of heat from the interior becomes insignificant in comparison with the energy received from the Sun, and the Earth has settled into a state where the climate is determined by much the same processes that determine today's climate: a competition between the rate at which energy is received from the Sun and the rate at which energy is lost to space by radiation of infrared light. This is very likely to have been the case by 4.4 billion years ago, if not earlier. There are no actual rocks as old as this, but there are individual zircon crystals embedded in the Jack Hills formation of Western Australia which are 4.4 billion years old. Zircons of a similar age are also found within the 3.7-billion-year-old crustal rocks of the neighboring Narryer Gneiss Complex. These crystals provide indisputable evidence for the existence of at least some continental crust of a sort very like that we see today; they also provide convincing though less certain evidence of the existence of liquid water in contact with the early continental crust. The existence of liquid water does not in itself put much constraint on temperature, since water can be maintained in a liquid state even at temperatures in excess of 500 K, provided the pressure exerted by water vapor in the atmosphere is high enough. The thermodynamics needed to address this issue will be introduced in Chapter 2. Certain aspects of the chemical composition of the zircons, however, suggest that they interacted with near-surface water having a temperature of 100 °C or less. By 4.4 billion years ago, it would appear, the Earth was no longer a molten volcanic inferno.

The precise nature of the climate evolution between 4.5 and 3.8 billion years ago is obscure at present. Depending on the composition of the atmosphere, the surface temperature could have been as high as 200 °C or low enough to cause the ocean (if any) to freeze over completely, and the climate could well have swung wildly between the two extremes. In addition, the dates of lunar craters indicate that the Earth very likely underwent a period of heavy bombardment by interplanetary debris between 4.1 and 3.8 billion years ago; it is generally supposed that this *late heavy bombardment* affected the rest of the inner Solar System as well, though that is far from certain. The energy brought in by impacts during this period could easily have been sufficient to bring surface temperatures episodically to values well in excess of 100 °C, sterilizing any nascent ecosystems. Life, if any, may have waged and won a battle for survival in deep ocean refugia.

By 3.8 billion years ago, the veil begins to lift. This is the age of the oldest intact rocks, found today in the Isua Greenstone Belt of Greenland. The appearance of these rocks marks the end of the *Hadean eon*, and the dawn of the *Archean eon*. Remnants of 3.7-billion-year-old shales in the Isua formation show the unmistakable signs of deposition of sediments in open water. More intriguingly, these shales are rich in organic carbon, and this carbon preserves a chemical signature generally associated with microbial activity – life. The Barberton formation of South Africa and the Warrawoona formation of Australia, both about 3.5 billion years old, contain layered carbonate sedimentary structures known as *stromatolites*, which in later times are known to be laid down by microbial mats. This is not an unambiguous sign of life, since inorganic processes can also produce stromatolite-like features. Be that as it may, the early stromatolites certainly require ponds of open water evaporating into air. The Barberton and Warrawoona formations also contain microscopic features that are suggestive of bacterial fossils, though not unambiguously so.

The record of surface conditions during the subsequent billion years is hardly continuous, but preserved rocks dating to this period very commonly show a sedimentary character of a type most easily explained by deposition in an open, unfrozen ocean. The first truly unmistakable microbial fossils date to 2.6 billion years ago, where they are found in the Campbell formation of Cape Province, South Africa, and argue for open water conditions having a moderate temperature. At about this time, we bid farewell to the Archean eon, and enter the *Proterozoic eon*, which extends to the appearance of animal life 544 million years ago. Certain fine-grained silica based sedimentary rocks known as *cherts* preserve information about past temperatures, as well as a wealth of fossils. Very ancient cherts contain no unambiguous microbial fossils, but certain aspects of their chemical composition point to temperatures as high as 70 °C at 3.5 billion years ago, declining to 60 °C at 2 billion years ago, and declining further to 30 °C at 1 billion years ago. Well-preserved ancient cherts are rare, however, so this data by no means implies that temperatures were uniformly warm on the young Earth. It only indicates that the Earth attained high surface temperatures at least part of the time; there is ample room to hide lengthy cold periods within the gaps in the chert record, as we shall soon see.

The earliest geological indication of the presence of glaciers on Earth occurs in the upper part of the Pongola formation of South Africa, and dates to 2.9 billion years ago. The evidence consists of glacial sedimentary deposits called *diamictites*, material of a sort usually transported by floating ice, and even glacier-scratched rocks. This does not mean that there were no earlier glaciations, but in light of the chert record and widespread occurrence of marine sedimentary rock it seems fairly certain that the Earth did not spend the bulk of its earlier history locked in a deep-freeze. Still, the Pongola glaciation seems to mark the beginning of Earth's long flirtation with ice. The Makganyene glaciation beginning around 2.3 billion years ago, recorded in rocks of the Transvaal group of Southern Africa, was a big one, and may well have been global. We know this because a record of the Earth's magnetic field is preserved in the rocks, and this can be used to infer the latitude at which the rocks were located when the glacial deposits were laid down. This *paleomagnetic data* shows that there was ice within 12 degrees of the Equator, strongly suggestive of a global glaciation.

The first unambiguous bacterial microfossils (found in the Campbell group of South Africa) date to 2.6 billion years ago, shortly before the Makganyene glaciation. While earlier fossil and geochemical evidence is very strongly suggestive of life, the Campbell group fossils are the ocular proof that biology was well under way. These fossils mark a watershed in another important way, in that they are identifiable as *cyanobacteria* – the type of organisms that produce oxygen by photosynthesis. The issue of when cyanobacteria evolved is hotly debated, with some lines of indirect evidence putting their appearance early in the Archean and others dating their onset to the time of the Campbell group microfossils. Be that as it may, the appearance of these fossils speaks for a fairly benign environment, with open water and temperatures no more than about 40 °C. After the Makganyene glaciation, microbial fossils become quite abundant. The two-billion-year-old Gunflint Chert of Canada is one of many such marine sedimentary formations in which cyanobacterial microfossils are preserved.

So far, no glaciations have been reported in the period between two billion years ago and 800 million years ago, though there are abundant sedimentary rocks dating to this time. The record is far from continuous and the lack of glaciations in this period may be an artifact of preservation, but the evidence certainly indicates that icy climates were not dominant at this time, and were probably quite rare. The long hiatus in ice is terminated by the massive – and possibly global – Snowball Earth glaciations of the Neoproterozoic, about 700 million

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years ago. Thereafter, the climate alternated between fairly lengthy periods when the Earth was ice-free or nearly so, and periods when there was at least some ice in polar regions. The ice never again, however, reached the nearly global proportions it attained during the Neoproterozoic, suggesting that the Earth passed some new threshold of climate stability in the Neoproterozoic. What might that be? This is one of the central questions of climate science.

Our overall picture of Earth history is that liquid water and moderate temperatures appeared at least episodically very shortly after the Moon-forming collision, and that the next three billion years had widespread open water with temperatures probably not exceeding 70 °C and generally much less. These conditions were punctuated by occasional glaciations, only a very few of which may have been global in extent. It was an environment that could support the evolution and survival of life, including (by 2.6 billion years ago, if not before) photosynthetic life requiring moderate temperature conditions. Let's keep this picture of relative stability in mind as we go on to discuss long-term changes in the atmosphere and the Sun – the two principal ingredients determining the Earth's climate, or indeed that of any planet.

There are many processes at play that cause the composition of a planet's atmosphere to evolve over time. In the earliest times, bombardments can help supply atmosphere-forming volatiles such as water, nitrogen, and carbon dioxide. Equally, however, sufficiently energetic bombardments can cause loss of atmosphere through literally splashing it into orbit. On a volcanically active planet with a hot interior, such as the Earth or Venus, or the younger Mars, new atmosphere is continually being supplied by outgassing of volatile substances from the interior of the planet. The heat needed to keep the interior of the planet churning so it can recycle minerals formed at the surface and cook out volatile gases in the hot interior is supplied by leftover heat from formation of the planet and by radioactive decay. How long this process can continue before the planet freezes out and becomes tectonically inactive depends on the size of the planet and the stuff it is made of; the nature of the gases which come out of volcanoes and other types of vents depends on the chemistry of the planet. For example, the early segregation of iron in the Earth's core made it harder to bind up oxygen in minerals, and therefore resulted in fairly oxidized gases like carbon dioxide (CO_2) and sulfur dioxide (SO_2) being released in preference to gases like methane (CH_4) and hydrogen (H_2) – though some of the latter two do nonetheless escape. The interior Earth also outgasses water vapor (H_2O), which is cooked out of hydrated minerals; the volume of the oceans appears to have been in a steady state for a long time, though, indicating that the rate of release is balanced by the rate of formation and subduction of new hydrated minerals at the surface. Nitrogen (N_2) is fundamentally different from other current and past constituents of the Earth's atmosphere as it does not readily get incorporated into the minerals that form the bulk of Earth's crust and interior. Unlike, say, CO_2, nitrogen does not cycle through the Earth's interior. The bulk of the Earth's N_2 is in its atmosphere and stays there, where it has probably been for almost all of our planet's history. This is likely to be the case as well for any other rocky planet made of stuff similar to the Earth – iron, oxygen (mostly bound up in minerals), silicon, magnesium, and sulfur.

While atmosphere is being supplied by outgassing from the interior, other processes cause material to be lost from the atmosphere. Parts of a planet's atmosphere extend far out from the surface, where hot, fast-moving molecules can reach escape velocity and escape to space. Besides escape from random molecular motions, the solar-heated tenuous outer atmosphere can sustain fluid flows which cause atmospheric mass to fountain systematically into the void. In addition, the solar wind can literally blow away the outer portions of an atmosphere; the extent to which this happens is affected by the intensity of the planet's magnetic field, which shields the atmosphere from the solar wind. As outer parts of the atmosphere are eroded, new gases from lower altitudes well up to replace the lost material, sustaining the gradual loss of atmosphere. All three mass loss processes preferentially remove lighter molecules, either because lighter molecules move more swiftly for a given temperature, or because the outer atmosphere is enriched in gases having a lower molecular weight. For a given density, a smaller planet has lower surface gravity, and so binds its atmosphere less tightly; in consequence, escape of atmosphere to space proceeds more rapidly on a small planet. Impacts by large, swift bodies can impart sufficient energy to part of the atmosphere to blast it into space. This mechanism of atmosphere loss does not discriminate as to molecular weight, but as with the other mechanisms, it is easier for a small planet to lose atmosphere this way. Overall, the Moon or Mars is more prone to lose atmosphere than more massive bodies such as the Earth or Venus, to say nothing of Jupiter or Saturn. For Earth and Venus, escape to space is significant only for H_2 and He, and of these the latter is important only as an indicator of planetary history rather than as a physically or chemically active component of the atmosphere. Saturn's satellite Titan is an interesting case, as it maintains a mostly N_2 atmosphere more massive than that of Earth (per unit surface area) despite having a surface gravity lower than that of the Moon. The very cold temperature of Titan helps it retain its atmosphere, but it is nonetheless likely that the persistence of the atmosphere requires a substantial rate of resupply from the interior of the planet.

Some components of the atmosphere can also be lost through chemical reactions with rocks at the Earth's surface. A particularly important example of this is the class of reactions commonly known today as *Urey reactions*,[3] which remove CO_2 from the atmosphere. When CO_2 dissolves in water, it forms a weak acid (carbonic acid), which reacts with silicate minerals (e.g. $CaSiO_3$) to form carbonate minerals (e.g. $CaCO_3$, or "limestone"). The reactions that form carbonate take place only in the presence of liquid water, so if a planet becomes so hot that liquid rain never reaches the surface, or if it somehow loses its water altogether, then CO_2 outgassed from the interior of the planet will accumulate in the atmosphere until the interior source is depleted or the rate of supply is balanced by loss to space. On Earth, all of the CO_2 presently in the atmosphere could be removed by the Urey reactions within 5000 years, forming a layer of limestone a mere 5 millimeters thick; if all the carbon stored in ocean water were to outgas as CO_2 and react to form limestone, the process would take a half million years and form a layer a half meter thick.

Life itself, once it appears, has a profound effect on atmospheric composition. While little methane escapes directly from the Earth's interior, bacteria known as *methanogens* can synthesize it from H_2 and CO_2 or from organic material produced by other organisms. Methanogens may well have dominated the ecosystems of the Earth's first two billion years, potentially allowing a methane-dominated atmosphere to build up. The advent of life also had a profound effect on nitrogen cycling. The bonds holding together N_2 are so strong that

[3] The reactions are named after the University of Chicago geochemist Harold Urey, who discussed them in a 1952 book called *The Planets: Their Origin and Development*. Although modern science was made aware of the importance of these reactions through Urey's work, the reactions were first introduced by the French chemist and metallurgist J. J. Ebelmen more than a century earlier. Ebelmen also introduced the notion that the silicate/carbonate reactions play an important role in determining atmospheric CO_2 and hence Earth's climate. Similar ideas were independently rediscovered by the Swedish geochemist A. G. Högbom in 1894, and then finally by Urey. For more details of the history see Berner 1996: *Geochim. Cosmochim. Acta.* **60**, 1633–1637.