Making It Comfortable

Running Water, Temperature Control, and Sun Protection

The solar system is marked by temperature extremes, from the millions of degrees of the solar corona to the near absolute zero of interplanetary space. The moon has temperature variations of ~300°C between lunar night and lunar day. Although Venus is nearly equal in size and bulk composition to Earth, the Venusian ground surface is 450°C warmer. Mars is 80°C colder. None of these environments are able to host liquid water, which is a critical need for life as we know it. Earth, in contrast, has a "goldilocks" temperature, with evidence for continuous liquid water at the surface for all of Earth's history recorded in the rock record. During this time the luminosity of the sun has brightened by about 30% as the sun has consumed its hydrogen fuel. How did this equable climate come about? When did it begin? How has it been maintained?

Earth's climate stability is dependent on its volatiles. The volatile budget of a planet depends on its accretion history and bulk composition, the amount of volatile loss to space from impacts and the solar wind, and the cycles of the volatile elements between planetary interior and exterior. Once the core formed a few tens of millions of years after accretion, Earth would have developed a magnetic field that deflected the solar wind, minimizing its effects on the atmosphere, preventing volatile loss, and protecting the surface from ionizing radiation harmful to life. Liquid water was present very early in Earth's history. Sediments, formed by deposition from water, and pillow basalts, solidified lavas that formed in contact with water, are present in the oldest rocks at 3.8 Ga. There is evidence for even

earlier liquid water from tiny crystals of zircon that have ages as old as 4.4 Ga. Climate stability is a long-standing characteristic of Earth's evolution.

A planet's surface temperature depends on the luminosity of its star and on the planet's distance from the star. It also depends on the reflectivity of its surface and on the "greenhouse power" of its atmosphere, caused by molecules consisting of three or more atoms, such as CO_2, H_2O and CH_4. Earth and Venus exemplify the importance of the greenhouse effect. Most Venusian carbon is in the atmosphere as CO_2, creating a powerful thermal blanket. By contrast, Earth's carbon is nearly all stored in sediments as carbonate minerals and organic residues. Feedbacks must have modulated greenhouse gases in the atmosphere to maintain long-term climate stability. The most likely feedback is a "tectonic thermostat" that relates subduction and volcanic outgassing of CO_2 to changes in weathering. High CO_2 or high temperatures enhance weathering that releases Ca^{2+} to the oceans. This then leads to cooling caused by removal of CO_2 as $CaCO_3$. Low CO_2 or low temperatures permit greater buildup of CO_2 from volcanoes, causing warming. Weathering is itself influenced by plate movements and mountain building. Hence, Earth's climate reflects linkages among the sun, plate tectonics, and surface biogeochemical cycles, providing climate stability consistent with liquid water. The tectonic thermostat depends on the coexistence of ocean and continent. Earth's surface has just the right amount of water for this balance. Whether this is a happy accident or the result of feedbacks in early planetary history remains an unsolved puzzle.

Introduction

We have yet to consider the attribute of our planet most important to living organisms—a stable climate that permits water on the surface. What fixes its water supply? What sets the temperature of its surface? What permits the lucky coexistence of continents and oceans? In a nutshell, what makes our planet habitable?

There are, of course, no simple answers to these questions. In previous chapters we have seen that the habitability of our planet is in part determined by its nebular heritage that sets its size, orbit, spin, and bulk chemical composition. It is in part determined by the evolution of its interior and crust. As we shall see in this chapter, it also critically depends on what happened to its volatiles after planetary accretion, and how they are cycled through planetary processes.

The Planetary Volatile Budget

For life of any complexity to develop on a planet, abundant liquid water must be available. Water is essential for all of life as we know it. Water is a fundamental medium of transport and chemical communication that make cellular processes possible. Living cells are about 70% water by weight. The average human being is 60% water (watermelon is >90% water). Water's centrality to life is reflected in the stark differences we see from region to region related to water availability. Given abundant rainfall, we have lush forests teeming with all manner of living organisms. Where there is little rain, we have deserts sparse in life. Where only snow falls, we have barren ice caps. These contrasts are found on a planet whose surface is 70% covered by liquid water!

Carbon is also essential for habitability, since it is the central element for all the organic molecules (those with C-H bonds) of which life is made. As we will see later in this chapter, C as CO_2 is also a pivotal molecule for climate stability, and its exact concentration in the atmosphere is a fundamental control on surface temperature. The *carbon cycle* links the carbon in organic molecules, the atmosphere, the oceans, the mantle and limestone ($CaCO_3$) in a balance that supports both life and the climate that is essential for life. For a habitable planet, the right amounts of H_2O and CO_2 are both critical.

Given the centrality of H_2O and CO_2, the first requirement for habitability is that the planet must have captured enough volatiles, including sufficient water to make a sizable ocean. The silicate earth as a whole contains only small amounts of H_2O and CO_2—about 700 ppm H_2O (0.07 wt.%) and 200 ppm CO_2 (0.02 wt.%). For H_2O these small amounts mean that Earth ended up with only one water molecule out of every

three million that were in the pool of matter from which Earth formed. Most of the carbon in the nebula was in the form of methane gas. Earth, however, somehow managed to capture about one in every 3,000 carbon atoms. These numbers further illustrate that Earth is very volatile depleted relative to the solar nebula. A curious fact is that the ratio of H_2O/CO_2 in the silicate earth (~3.5) is significantly higher than the ratios in chondrites (H_2O/CO_2) <1.5. One solution would be that much of Earth's volatile budget comes from comets, which have a high H_2O/CO_2 ratio. Or carbon may be one of the light elements in the core. Water and CO_2 are further pieces to the puzzle of the origin of Earth's atmosphere and ocean prior to the beginning of the rock record.

The small amounts of volatiles in Earth as a whole lead to the second habitability requirement—given a modest volatile budget, the volatiles must be concentrated at the surface. This occurred on Earth, since at the surface a low volatile budget is not at all evident. To the contrary, the proportion of H_2O and CO_2 in the combined atmosphere, ocean, and crust is rather high—7.2 wt. % H_2O and 1.5 wt. % CO_2. These numbers reflect ~100 times enrichment relative to the total planet and are just the right amounts for a large liquid ocean and climate stability conducive to life. At the high temperatures that must have prevailed during the period of the formation of our iron core, extensive melting and active convection would have cycled mantle rocks to the surface, where their H_2O and CO_2 would have been transported to the atmosphere in gaseous form. As the iron migrated to the core, H_2O and CO_2 would have migrated to the surface. It is also possible that volatiles degassed during impacts of incoming planetesimals, so that volatiles were preferentially accreted at the surface.

Sufficient volatiles at the surface, however, are not all that is required for habitability. The water at the surface must be in liquid form. Can we somehow ascertain when liquid water, essential for the formation of life, might have first appeared? The answer to this question is critical for the origin of life, discussed in Chapter 13, because it constrains the time interval over which the processes leading to life had time to operate. For example, if life and liquid water appeared at the same time, then life's origin would be geologically instantaneous. If water were present from the beginning, life could have a billion years or more to develop. Which is it?

Fig. 9-1:
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courtesy

Evidence for Liquid Water before 4.0 Ga

Some of the oldest rocks are sedimentary rocks, and most sediments require weathering, transport ,and deposition by liquid water. The evidence for the earliest fossils comes from rocks that are 3.5 billion years old. The oldest sediments are those of the 3.8 Ga Isua formation in Greenland. These rocks include cherts, carbonates, and banded iron formations. All of these rocks require liquid water to form, and the same rock types occur in much younger rocks when we know liquid water was present. The rocks show that water was present at least as early as 3.8 Ga.

We are able to push back the presence of liquid water even earlier by using evidence from a surprising source, the mineral zircon ($ZrSiO_4$)— one of the highest-temperature and most stable minerals found in rocks. Zircon is very low in abundance (usually less than 0.02% of the rock), but also very common. Virtually all granites and sandstones contain some grains of zircon. Zircons are also very stable minerals and are difficult to alter or dissolve. The high chemical fidelity and chemical resistance of zircons allows them to survive during weathering and sedimentary transport; they are so robust they often survive even multiple melting
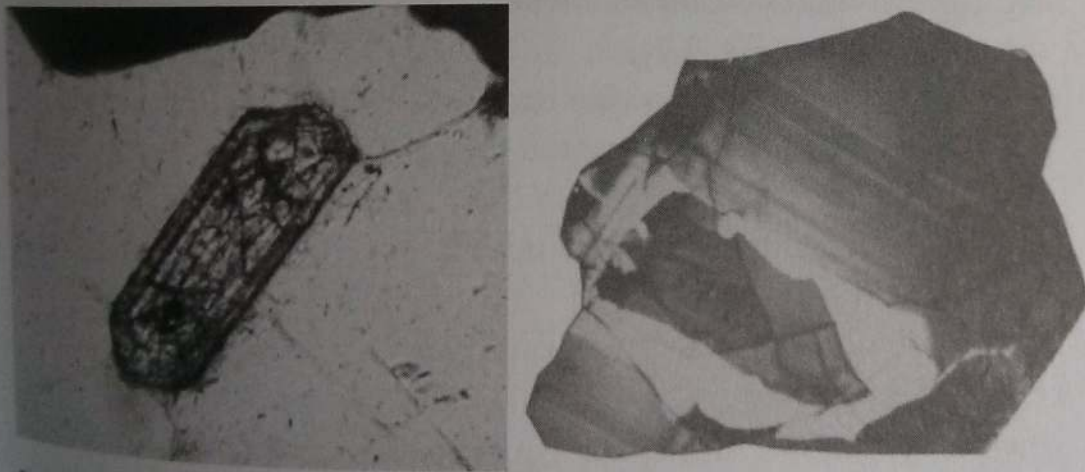

Fig. 9-1: Images of zircons. *On the left*: A single zircon crystal in a biotite. The crystal is about 100 microns (1/10 mm) in length. *On the right*: A zircon viewed under cathode luminescence that reveals its zoning and growth history. Each point in a zircon can give a precise date using the U-Pb system, (see Fig. 9-2). The zircon has a complex history, with an old inner core that was partially corroded, surrounded by younger generations of mineral that grew around it. The old core has an age of 4.4 Ga, the oldest age found for any terrestrial material. (Photograph courtesy of John Valley)
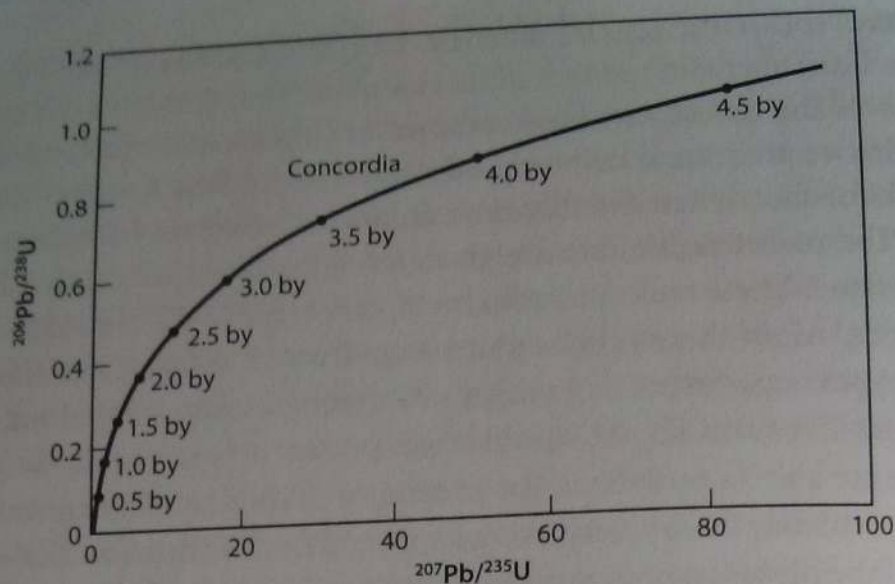
Fig. 9-2: The "Concordia" diagram used to illustrate U-Pb dating that is possible with zircons. Zircons contain no Pb initially, so all the Pb is created by radioactive decay of the two isotopes of U. Because the half-life of ^{235}U is much shorter, much more ^{207}Pb is created in older rocks than in younger rocks. Samples that have not lost any Pb since they formed will plot on the Concordia, and their age is confirmed by two independent methods. Pb loss causes the data to move directly toward the origin at the time the Pb loss occurred. This can also be used to constrain ages, an original age and a metamorphic age when the Pb loss occurred.

events, creating zoned minerals where each part of the mineral formed at a different time (Fig. 9-1).

Zircon has one other key characteristic—mineral grains can be individually dated. Zircon concentrates the parent element U and excludes the ultimate daughter element Pb. These are the ideal initial conditions for radiometric dating. Furthermore, ^{238}U and ^{235}U have different decay constants and decay to ^{206}Pb and ^{207}Pb, respectively, so that two ages can be determined independently. Because of the different decay constants, relatively more ^{207}Pb is formed at the beginning and more ^{206}Pb more recently. If Pb is lost during subsequent geological processes, all the Pb isotopes are lost proportionally, and the ages no longer agree. When they do agree, the age is robust and the zircon is said to be *concordant* (Fig. 9-2). Zircons are thus very effective messengers from the past, because they record the time of their formation and they resist subsequent chemical change.

These characteristics make ancient zircons the oldest Earth materials that have not been modified since earliest Earth's history. The most an-

cient zircons are preserved in Archean sedimentary rocks. These rocks are as old as the igneous rocks that surround them, but the sedimentary rocks, particularly sandstones, preserve zircons that were created by a previous generation of igneous events and then were preserved during weathering to survive in the younger sediment. The most famous locality for such ancient zircons is an apparently nondescript sedimentary rock in Australia, called the *Jack Hills formation*. This formation has been exhaustively studied, and zircons have been recovered with concordant ages as old as 4.4 billion years. This is much older than the oldest known rock with a reliable date associated with it—the Acasta gneiss, near 4.0 Ga. So how do these little minerals tell us about ancient water?

Zircons provide evidence for the early presence of water through two fairly detailed lines of reasoning. Water has a strong influence on freezing point depression and permits melting of Earth materials at low temperatures. The lowest temperature silicate melt is granitic magma, which can be produced by hydrous melting of basalt, sediment, or other granites. Higher-temperature magmas also differentiate toward granitic compositions, as they crystallize in the presence of water. Granites imply water. While zircons can be found in anhydrous mafic rocks, they are rare. In hydrous granitic rocks they are ubiquitous. The common existence of zircons in the Jack Hills formation suggests granites, which requires water. This is not quite proof, however, since some zircons also occur in high-temperature, anhydrous magma.

Further evidence comes from the trace element contents of zircons. Titanium is incorporated as a trace element in zircon because it has the same 4+ valence state as Zr. Bruce Watson and Mark Harrison showed that the amount of Ti incorporated in zircon is very sensitive to temperature. Measured Ti contents of the Jack Hills zircons show that they formed at temperatures of about 750°C, a temperature associated with hydrous, granitic magmas and not with anhydrous mantle-derived magmas. The zircons come from low temperature granites, which requires water. Granites are also the characteristic rock type of continents, so the data suggest continents were present as well.

STABLE ISOTOPE FRACTIONATION

Here we need a brief interlude to introduce the concept of *stable isotope fractionation*, which is a final line of evidence from zircons. In previous

chapters we have discussed variations in isotope ratios of elements resulting from radioactive decay. Oxygen is not a radioactive decay product, and all isotopes of oxygen have the same electron shell structure, so how could the ratios of oxygen isotopes vary? It turns out that at low temperatures, processes discriminate slightly among isotopes of the same element based on their mass. The variations are so small that they are reported as parts per thousand (or "per mil") relative to a seawater standard. One consequence of this isotopic fractionation is that rainwater that falls on continents—i.e., has a slightly higher ratio of $^{18}O/^{16}O$. In order to make the numbers a bit more intuitive, stable isotope variations are always referred to as "per mil" variations relative to a well-known standard, with the heavier isotope in the numerator and the light isotope in the denominator. For oxygen the standard is mean seawater. The notation used is $\delta^{18}O$, so seawater has a $\delta^{18}O$ value of 0 per mil. "Heavy" oxygen with higher $^{18}O/^{16}O$ than seawater has positive values of $\delta^{18}O$ (e.g. 10 per mil would be 1% heavier than seawater).

The mantle has $\delta^{18}O$ of about 5 per mil, as indicated by the oxygen isotope measurements of mantle materials reported in Figure 9-3a and 9-3b.

Rocks that have been influenced by a low-temperature water cycle involving evaporation and precipitation (i.e., weather with a liquid ocean) have heavier oxygen, with $\delta^{18}O$ greater than $+5$. This interaction can involve either sediments in the source regions that melted to produce the rocks or interactions with migrating fluids in the crust that are derived from rain. In either case, a low-temperature water cycle is indicated. We can see the evidence of this water cycle by examining data from rocks when we know a water cycle was present. For example, some igneous rocks are known to be formed from sediments that require a water cycle. These can be seen in Figure 9-3c as the "metasedimentary province plutons" with $\delta^{18}O$ of 6 to 7. So are the Jack Hills zircons from sedimentary or mantle-derived materials? The Jack Hills zircons are isotopically heavy, very similar to continental zircons formed in modern times (Fig. 9-3). The heavy oxygen suggests an active low-temperature water cycle was present during the formation of the rocks whose zircons survived in the Jack Hills formation. Otherwise, the oxygen isotopes would not be fractionated.

The zircon evidence suggests that as far back as 4.4 billion years there was a robust water cycle on Earth, and liquid water was present. It is a beautiful piece of geological detective work that some of the smallest
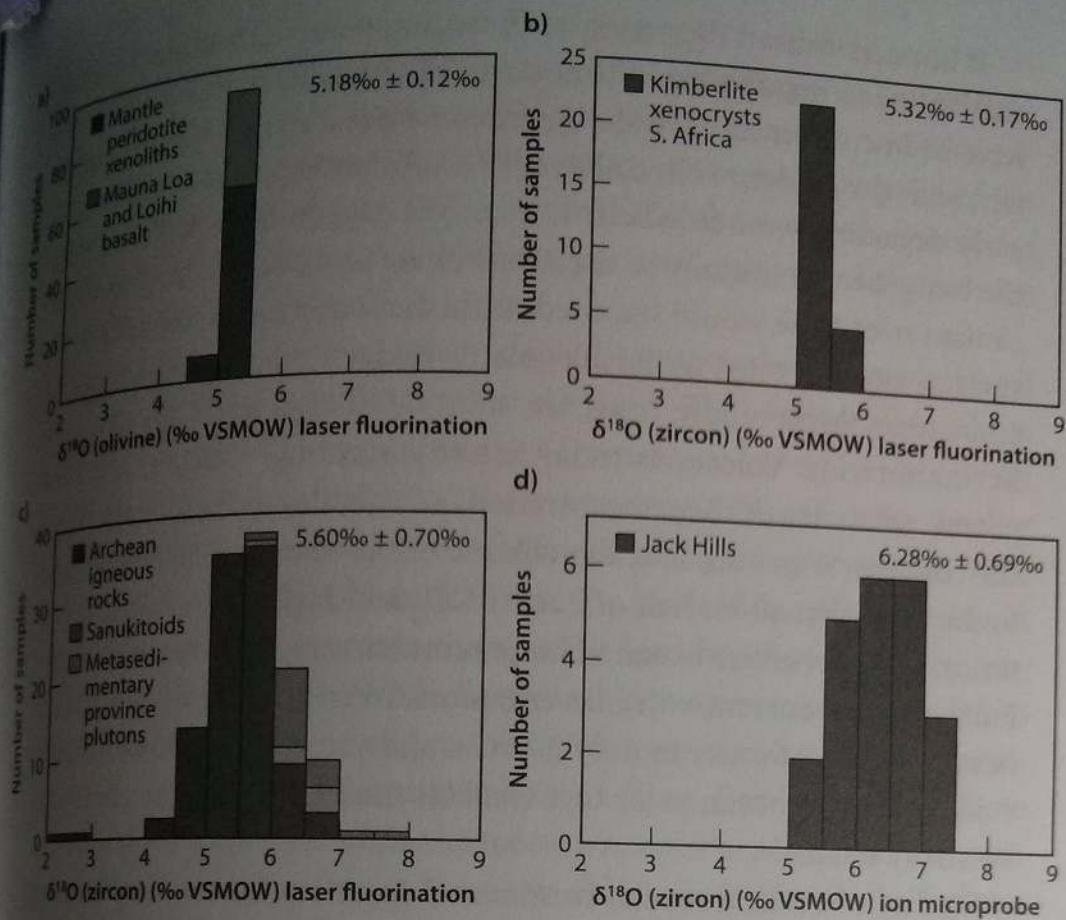
Fig. 9-3: Oxygen isotope data from various rocks compared to the data from the ancient zircons collected in the Jack Hills formation. The top two panels, a and b, show the data for mantle derived magmas which have had no interaction with the water cycle, with values of 5.2–5.3. The lower left panel c shows Archean igneous rocks are similar to mantle values, while sediments that have interacted with the water cycle have elevated values. The higher values of the Jack Hills zircons in panel d require that their source rocks had seen the influence of a low temperature water cycle. (Modified from J. Valley, *Reviews in Minerology and Geochemistry*, v. 53, no. 1, 343–385)

and rarest mineral grains found in rocks hold the essential clues to water's presence, providing crucial evidence for appropriate conditions for life's origin.

Controls on Volatiles at the Surface

For habitability over Earth's history, we need to consider the long-term controls on the total amount of water and carbon at the surface—not how the volatiles cycle through surface reservoirs over a few thousand years or less, but how they cycle between the interior and exterior over hundreds of millions of years.

If impacts caused degassing of incoming planetesimals, or core formation led to massive early degassing of Earth's interior, volatiles would have been concentrated to the surface in earliest Earth's history, consistent with the evidence cited above for a substantial ocean at that time. If early degassing were so efficient, we might expect much of Earth's volatile budget to be initially in the atmosphere and ocean. Continued volcanism over time would have led to further addition of volatiles to the surface, causing most of Earth's volatile budget to be in the atmosphere and ocean. Surprisingly, however, substantial H_2O and CO_2 remain in Earth's interior. Volcanoes today are still emitting volatiles, and these permit estimates of the concentrations of volatiles in the mantle. While the concentrations are low, the volume of the mantle is so large relative to the crust that about half of Earth's CO_2 and H_2O still reside in the interior. Another entire ocean volume remains trapped in the solid Earth. Furthermore, current volcanic emissions over time would generate an ocean volume of water in only 2–3 Ga, and yet as we saw above there is evidence for an ocean prior to 4 Ga. Has the ocean then increased substantially in size?

Studies of rocks from the continental crust can be used to show that sea level has remained remarkably constant through Earth's history, implying near constancy of the volume of the oceans and hence water at the surface. Since volatiles (including H_2O) are steadily being supplied from Earth's interior, how can the volume of H_2O at the surface have remained in a narrow range? And since degassing is an inevitable result of early Earth's history and continued volcanism, how can so many volatiles remain in Earth's interior?

These questions require a consideration of the surface volatile budget, not just as a progressive degassing but also as a dynamic process involving fluxes among Earth's reservoirs and space, causing volatile addition and removal. Water and CO_2 removal could occur by volatile loss to space or by returning H_2O and CO_2 to the interior during recycling of Earth's plates.

ATMOSPHERIC LOSS TO SPACE

Once at the surface, any gaseous substance has the opportunity to escape into space. The most well known mechanism is called thermal escape.

Just as a space vehicle can escape Earth's gravitational field with suffi-cient velocity, individual atoms or molecules can escape when their ve-locity is high enough. Velocities increase with temperature and decreas-ing atomic mass. For Earth the temperature of the outer regions of the upper atmosphere is about 1500°K, while that at the surface is only about 300°K. The high temperatures of the upper atmosphere greatly increase the probability for molecular escape.

The velocity required for escape depends on the planet's gravitational field and on the mass of the molecule itself. These dependencies are extremely strong. The escape velocity from Jupiter is 60 km/sec, from Earth it is 11.2 km/sec, and from the moon only 2.4 km/sec. For smaller planets, the escape velocity is much lower, and gases can escape more easily. Escape also depends critically on the mass of the gas molecule. A factor-of-2 difference in mass changes the likelihood of escape by sev-eral orders of magnitude. While Earth and Venus are massive enough to prevent thermal escape of all but the lightest gases, the moon has insuf-ficient gravity to hold even the heaviest gas. Thus, Earth and Venus have substantial atmospheres while the moon has none at all. Jupiter has such a high escape velocity that it has been able to retain even the lightest gases, hydrogen and helium. Planet size and the ability to retain an at-mosphere are critical for habitability.

There are other mechanisms of atmospheric loss. Particles of the solar wind can have very high velocities that can strip gases from the outer atmosphere. Impacts can also cause stripping of the atmosphere by ac-celerating molecules to escape velocities. And if planets are too close to their star, the very high temperatures can produce various effects that create atmospheric loss. The diversity of processes of atmospheric loss and how they change over planetary history may help to account for much of the diversity of planetary atmospheres and compositions in the solar system.

For our present purposes, however, we need to estimate to what ex-tent H_2O and CO_2 might be lost from Earth. By turning to the evidence from helium, we are able to estimate the extent these heavier gases have been lost. This method involves a comparison between the total number of helium atoms in the atmosphere and the number of helium atoms that leak into the atmosphere from Earth's interior each year (Fig. 9-4). The number in the air is obtained from the mass of the atmosphere and its
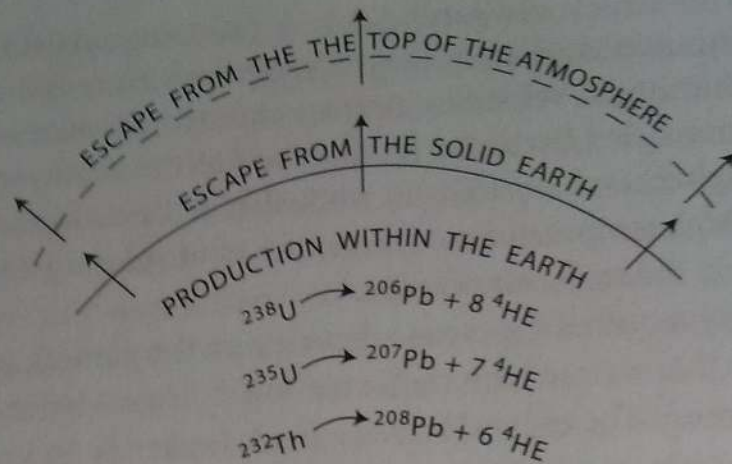
ESCAPE FROM THE THE TOP OF THE ATMOSPHERE

ESCAPE FROM THE SOLID EARTH

PRODUCTION WITHIN THE EARTH

$$^{238}U \longrightarrow {}^{206}Pb + 8\ {}^{4}HE$$

$$^{235}U \longrightarrow {}^{207}Pb + 7\ {}^{4}HE$$

$$^{232}Th \longrightarrow {}^{208}Pb + 6\ {}^{4}HE$$

Fig. 9-4: Earth history of helium atoms. ^{4}He atoms are generated within the Earth's crust and mantle by the decay of uranium and thorium. By measuring the amount of heat escaping from Earth, we have a fairly good idea of how much uranium and thorium are present in Earth. Thus we know the rate at which ^{4}He generation occurs. After a billion or so years of entrapment in solid Earth, the average helium atom manages to reach the surface, where it resides an average of 1 million years before escaping from the top of the atmosphere. All the helium atoms manufactured by radio decay within Earth are eventually lost to space.

helium content. Helium production at ocean ridges can be determined by measuring the helium concentrations in ocean ridge basalts, in the hydrothermal fluids at deep sea vents (discussed at length in Chapter 12), and in seawater. Since helium is produced by the radioactive decay of ^{238}U, ^{235}U, and ^{232}Th, estimates of these concentrations in continental rocks, combined with measuring heat flow on continents that is caused by radioactive decay, permit estimates of how much helium is escaping from continents each year. The number of atoms being added to the atmosphere in a year is about one-millionth the number of helium atoms currently residing in the atmosphere. This suggests that helium atoms reside in the atmosphere for an average of 1 million years before they escape from the atmosphere to space. Using the helium escape time, the escape time for the other gases can be calculated from molecular theory. With masses of 20 for neon, 28 for N_2, 32 for O_2, and 44 for CO_2, escape times are so long that atmospheric loss is negligible over Earth's history.

With its atomic weight of 18, water has a mass similar to neon, and therefore water molecules do not escape from the atmosphere. But the hydrogen atoms that are essential parts of the water molecule are a dif-

Table 9-1
Composition of Earth's atmosphere today*

Gas Name	Gas Formula	Percent by Volume
Nitrogen	N_2	78.08
Oxygen	O_2	20.95
Argon	Ar	0.93
Carbon dioxide**	CO_2	0.039
Neon	Ne	0.0018
Helium	He	0.00052
Krypton	Kr	0.00011
Xenon	Xe	0.00009
Hydrogen	H_2	0.00005
Methane**	CH_4	0.0002
Nitrous oxide**	N_2O	0.00005

*In addition, the atmosphere contains water vapor (H_2O) in variable amounts (up to 2% for warm air and down to a few parts per million for very cold stratospheric air). Water is also a greenhouse gas.
**Greenhouse gases.

ferent story. As H_2 is only half as massive as helium, hydrogen molecules have an escape time far less than 1 million years. Fortunately, H_2 is a very rare gas in our atmosphere (see Table 9-1).

Today any H_2 molecules generated by bacteria living in soils survive only a few years in the atmosphere before being converted to water ($2H_2 + O_2 \rightarrow 2H_2O$). There is another route, however, by which a planet can lose its hydrogen and hence its water. High in the atmosphere, ultraviolet light from the sun breaks H_2O molecules apart, creating free H atoms. These free H atoms are exceedingly vulnerable to escape. The O atoms left behind eventually react with either iron, sulfur, or carbon. This process is the likely mechanism by which Venus lost most of its water.

The reason why this process has not decimated Earth's water reserves is that our atmosphere has a "water trap" that keeps almost all of Earth's water in the lower atmosphere, preventing it from being carried to higher

UV light

Stratosphere
$H_2O = 5$

Troposphere
$H_2O = 30,000$

Lakes, rivers,
ground water...
$H_2O = 80,000,000$

Ice caps
$H_2O = 40,000,000$

Oceans
$H_2O = 2,700,000,000$

Solid Earth
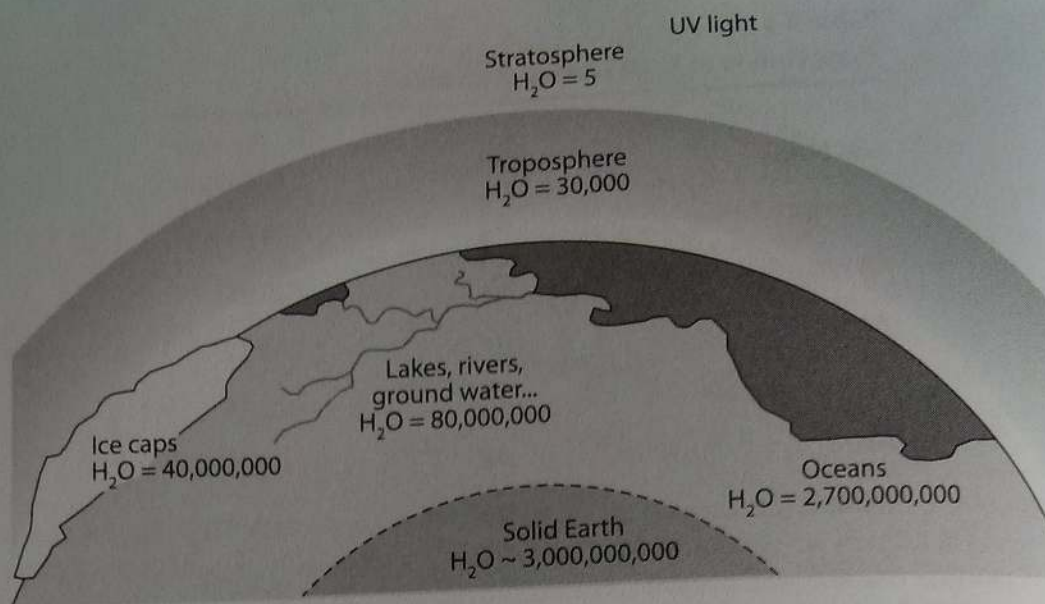$H_2O \sim 3,000,000,000$

Fig. 9-5: Most of Earth's hydrogen is in the form of water, about half of which resides in the ocean. The majority of the remaining water is trapped in solids making up the mantle and crust. Earth's freshwaters (lakes, rivers, groundwater, etc.) make up only about 3.0% of the total exterior water. Its ice caps make up only 1.5% of the total. Only a very small fraction of our water is at any given time stored in the atmosphere as vapor, which is confined almost entirely to the lower, well-stirred part of the atmo-sphere (referred to by meteorologists as the troposphere). Only two of every billion water molecules reside in the stratosphere. This is important, because only that water present in the stratosphere has a chance to be dissociated by ultraviolet light. Dashed line separates Earth's interior from exterior.

levels from which it could escape. As tallied in Figure 9-5, the bulk of our water resides in the ocean, sediments, and ice. At any given time only about one H_2O molecule in 100,000 is in the atmosphere. The lower atmosphere is called the *troposphere*, and as we all experience, the tem-perature in the troposphere declines rapidly with increasing height above sea level (Fig. 9-6). This temperature decrease with altitude causes water vapor to precipitate as dense ice crystals to form the clouds and snow. It can be a warm, sunny day in Los Angeles, California, or Nice, France, while snowing a short distance away in the mountains at heights of a few thousand meters. Airplanes flying at 10,000 m are at −60°C even on summer days. At the top of the troposphere the temperature is so cold (−60°C) (Fig. 9-6) that virtually no water vapor can exist, and only extremely dry air migrates from the troposphere to the next highest at-mospheric level, called the *stratosphere*. These attributes of Earth make
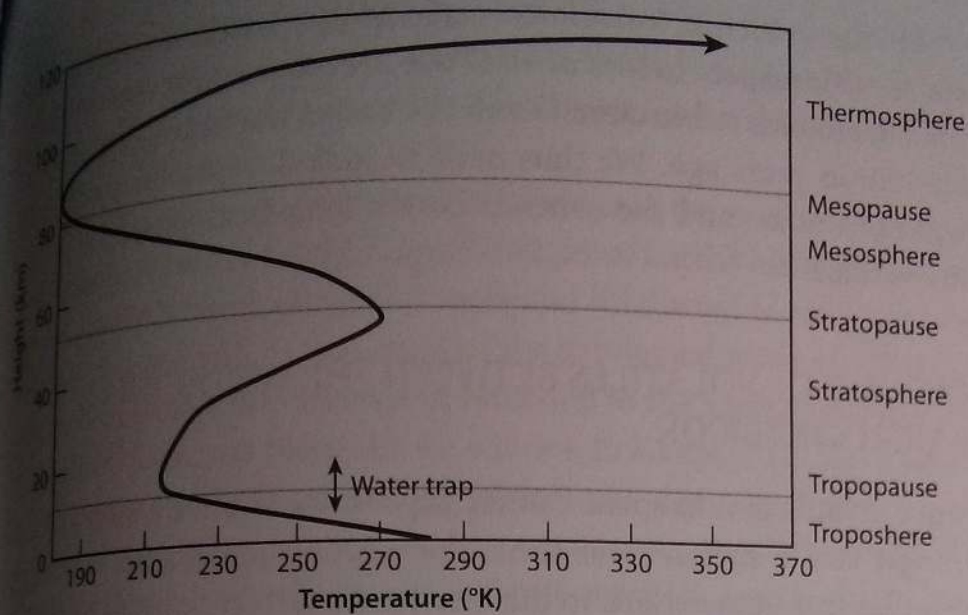
Fig 9-6: Temperature profile through Earth's atmosphere. All of weather occurs in the troposphere. At the top of the troposphere, temperatures are so cold that all water has precipitated as ice, and none migrates to the upper atmosphere where it can be broken apart, which would allow H atoms to escape.

its hydrogen escape hatch very small. Over the last 4.0 billion years where there is a rock record and evidence for liquid water, only a small fraction of our hydrogen has been lost!

Of course, what may have happened in earliest Earth's history is not so clear. In the early Earth there was no O_2 and bacteria likely converted hydrogen to methane ($4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$). While methane is in very low concentration in the atmosphere today, it might have been more abundant on early Earth, and there is no cold trap as there is for water, so methane would be able to rise to the upper atmosphere and be broken apart with loss of H. Massive impacts can also cause atmospheric loss even of heavier molecules, and very high atmospheric temperatures after the moon-forming impact would have had major effects on the atmosphere. Is there another way we can determine whether Earth lost a lot of its hydrogen?

Here once again stable isotope variations provide important evidence. Hydrogen has two isotopes, ^1H (called H) and ^2H (deuterium, or D), which is a factor-of-2 mass difference. This leads to *much* easier escape for ^1H relative to D. But Earth's D/H is about the same as chondrites, suggesting little hydrogen loss. Earth was able to retain its water.

All the evidence, therefore, suggests that Earth's atmosphere was stable with respect to loss of H_2O out the top, certainly by the time of the advent of a stable climate and the end of the largest impacts some 3.8 billion years ago. We thus need to look downward as well as upward to understand the controls on the long-term volatile budgets at the surface.

CYCLING OF VOLATILES BETWEEN THE SURFACE AND EARTH'S INTERIOR

Since volatile loss to space cannot explain the relatively constant water budget at the surface over time, the solution must lie in recycling of volatiles from the surface to the interior. Return of volatiles to the interior would also account for the significant amounts of volatiles that reside today in the mantle.

The process of volatile recycling is the subduction of Earth's tectonic plates, which will be discussed at length in Chapters 10 and 12. The new ocean crust formed at ocean ridges leads to extensive circulation of seawater through cracks in the crust. Interactions between the rocks and the water cause alteration of the crust to form new minerals that contain water and CO_2 in the solid state (e.g., sheet silicates and calcium carbonate.

Further alteration occurs as the spreading plate moves the crust away from the ocean ridge, and at the same time sediments fall through the ocean to create a progressively thickening sedimentary layers, including clays and carbonates made up of volatile-rich minerals. When the plate reaches the subduction zone, this volatile-rich package is "subducted" down into the mantle, returning volatiles to the interior. By this mechanism a flux from the surface to the interior balances the volcanic flux to the atmosphere.

Precise estimates of the down-going flux are difficult to obtain because no single drill hole has yet been able to penetrate the entire ocean crust, and only a few holes have been able to penetrate a kilometer or more. Considering the vast expanses of the oceans, and the diversity of ocean crust environments, our knowledge of the average composition of altered ocean crust is very limited. The data that do exist suggest that the ocean crust contains sufficient H_2O and CO_2 to easily balance the

volcanic outgassing and supply sufficient CO_2 and H_2O to the interior to explain the substantial amounts that reside there. In fact, so much H_2O goes down the subduction zone that if it all remained at depth the oceans would diminish with time!

It remains curious that the amount of water at the surface appears to have remained within a tight range throughout Earth's history. This implies a balance between outgassed water and subducted water. A possible solution to this puzzle is that most of the subducted water is efficiently processed at subduction zones and returned to the surface through the volcanism that occurs there. As we will see in Chapter 12, the volatile-bearing minerals of the subducting plate break down and release their volatiles at the high pressures and temperatures of Earth's interior. The released volatiles then trigger volcanism that transfers water to the surface. If more or less water were subducted, more or less outgassing would occur. The net flux of water in or out of the Earth could then be small enough that there would be little variation in total amount of water at the surface.

For CO_2, the budget is much less clear. Unlike water, where changes in sea level provide information about the surface water budget, there is no clear geological indicator of the amount of CO_2 at the surface over Earth's history. Carbonate minerals are also more stable than hydrous minerals in the subducting plate, and substantial amounts of CO_2 in carbonates could get past the subduction zone filter and returned to the mantle. Much remains to be understood concerning the overall CO_2 budget related to outgassing and subduction.

Surface Temperature

For the H_2O at the surface to be in the essential liquid state, the Earth's surface temperature must have been maintained within a narrow range. Our water would be of little use to life were it tied up in massive ice sheets. Nor would it be of use if it were all in the atmosphere as steam. And if temperature changed from near freezing to near boiling on a regular basis, life could also not survive. How has Earth's surface temperature maintained a narrow range consistent with liquid water over billions of years?

A planet's temperature depends not only on the amount of sunlight it receives but also on the reflectivity of its surface and on the content of so-called greenhouse gases in its atmosphere. If a planet had the surface properties similar to those of a *blackbody*, its temperature would be fixed solely by the amount of sunlight reaching its surface. To qualify as a blackbody, the surface of an object must be nonreflecting—i.e., all the sunlight reaching it must be absorbed and reradiated as infrared light (Fig. 9-7). Also, there can be no gases in its atmosphere that absorb outgoing infrared light. Were Earth a blackbody it would have a mean surface temperature of about 5°C (see Table 9-2).

No planet we know of, however, is a perfect blackbody. All have an *albedo* that indicates what proportion of the light is reflected. The higher the albedo, the more light is reflected and the cooler will be the planet. The reflectivity of a planet has much to do with the amount and state of its water. Ocean water has a low reflectivity; ice and clouds have a high reflectivity. As plant leaves absorb nearly all the light they receive, there is little reflection from a forest. By contrast, about half the light reaching bare soil is reflected. As we have already pointed out, the extent of plant cover depends on the distribution of rainfall. On Earth, clouds, ice caps, and soils reflect back to space a sizable portion of the sunlight impinging on Earth, leading to an albedo of about 0.3. Thirty percent of the sunlight is reflected back into space and plays no role in heating Earth's surface. Were this the only deviation from the ideal blackbody, Earth's surface temperature would average −20°C and all water would be frozen. High albedo lowers planetary temperature.

The factor that counterbalances albedo and warms a planet is the greenhouse effect caused by particular molecules of gas in the planetary atmosphere. All molecules with three or more molecules are greenhouse gases. Such molecules absorb energy of packets of infrared light through the vibrations of their molecular bonds (Fig. 9-8). Incoming solar radiation has short wavelengths that are not absorbed by greenhouse gases, so the energy makes it through the atmosphere to the surface. When the light is radiated from the surface, however, the wavelengths of light correspond with planetary temperatures of about 300 K and are largely in the infrared. These wavelengths are effectively absorbed by greenhouse gases. Important greenhouse gases in Earth's atmosphere are water vapor (H_2O), carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and

Table 9-2
Summary of the factors influencing the surface temperatures of the terrestrial planets

	Mass of atmosphere kg/cm²	Distance from Sun 10⁶ km	Solar energy received 10⁶ watts/m²	Black-body temperature °C	Fraction sunlight reflected	Reflective cooling °C	Green-house warming	Actual surface temperature °C
Mercury	0	58	9126	175	.068	−8	0	167
Venus	115*	108	2614	55	.90	−144	+553	464
Earth today	1.03**	150	1368	5	.30	−25	+35	15
Early Earth		150	958	−26	.30 (?)	−21	62(?)	15 (?)
Mars	0.016*	228	589	−47	.25	−16	+3	−60
Moon	0	150	1368	5	.11	−7	0	−160 – +130

*Mostly CO_2.
**Mostly $N_2 + O_2$.
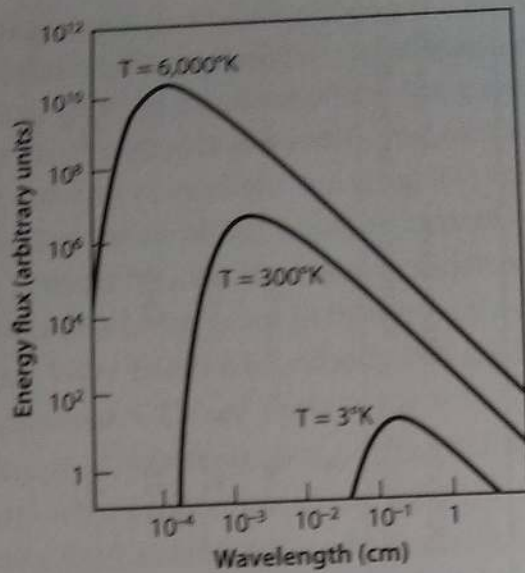
Fig. 9-7: Light emitted from blackbodies of three quite different temperatures: The hotter the body, the more energy it emits (the 6,000 K body gives off about 10,000 times more energy per unit area than the 300 K body and 100 million times more per unit area than the 3 K body). The wavelength representing the peak of energy emission for a star whose surface temperature is 6,000 K lies in the visible range, that for a planet whose surface temperature is 300 K lies in the infrared range, and that for a universe whose background glow temperature is 3 K lies in the microwave range. Earth's atmosphere is transparent to the short wavelengths of the sun's radiation but absorbs some of the energy of Earth's reflected radiation.

ozone (O_3). The capture of outgoing earthlight by these gases serves as a thermal blanket that keeps the planet warm. For Earth, the greenhouse warming more than compensates for the sunlight lost through reflection. Earth's mean surface temperature (i.e., 15°C) is 10°C warmer than if it were a perfect blackbody (see Table 9-2).

To assess another planet's surface temperature, we also need to know how much sunlight it receives, the reflective properties of its surface and the amounts of infrared-absorbing gases contained in its atmosphere. Solar radiation received is a straightforward function of distance from the sun. Albedo can be measured from space. Greenhouse effect can be determined where the composition of the atmosphere is known or can be adequately estimated. Table 9-2 shows how the combination of solar radiation, albedo, and greenhouse effect lead to a planet's surface temperature. On Earth, it is clear that habitability is strongly influenced by
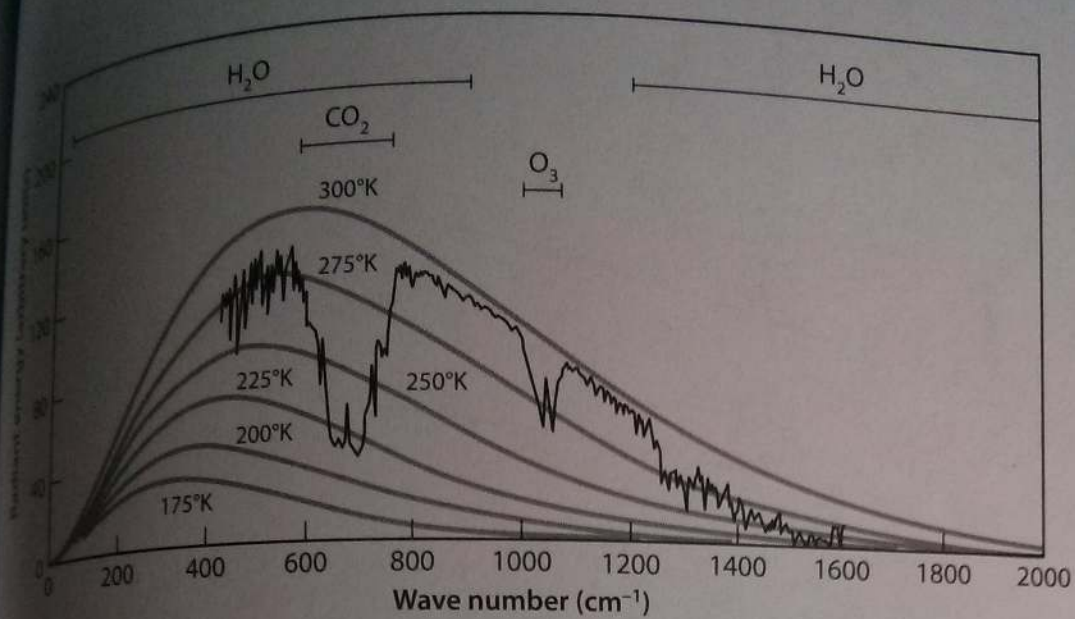
Fig 9-8 Absorption of outgoing Earthlight. The jagged curve shows an actual spectrum of Earthlight leaving the top of the atmosphere over the island of Guam. For comparison, the smooth curves are blackbody curves that show the expected spectra if there were no greenhouse gases. These curves are drawn for a series of temperatures; that appropriate for Guam would be just less then 300 K. The wiggles and large dips are the result of absorption of the radiation by water, carbon dioxide, and ozone in the atmosphere. Water creates a broad reduction in the region 400–600 cm^{-1} As can be seen, the dip created by CO_2 is especially prominent. The wave number is a measure of the frequency of the radiation.

the fact that the greenhouse warming is large enough to more than off-set reflective cooling.

Table 9-2 also shows the great importance of solar energy for a planet's blackbody temperature, which is the baseline upon which planetary temperature depends. Has solar energy been constant through time? While we have no direct measurements of long-term changes in energy coming from the sun, there is evidence from other stars in the galaxy at diverse stages of evolution that reveals how stellar energy production changes with time. Stars similar to the sun increase their energy output with time, as the hydrogen fuel in the interior converts to helium and increased temperatures are needed to balance the contracting forces of gravity. Astronomers estimate that the sun was producing about 30% less heat in Hadean times than it is emitting today. Using this luminos-ity, we can calculate the blackbody surface temperature of Earth for its early history, shown in Table 9-2 and illustrated in Figure 9-9.
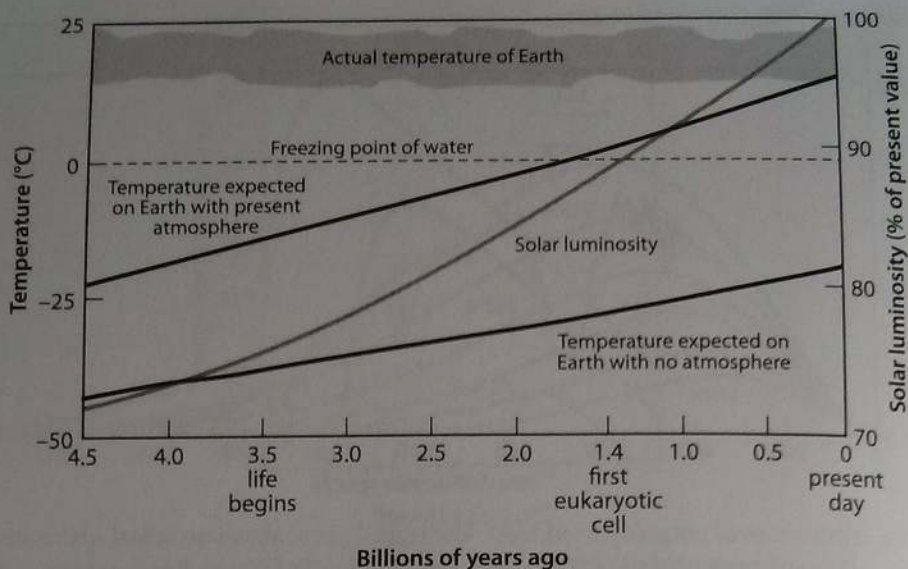
Fig. 9-9: Illustration of how the sun's luminosity has changed over Earth history and its consequences. The sun today is emitting 30% more energy than it was in the Hadean. In the absence of any greenhouse effect, Earth would have been below freezing throughout its history. With today's atmosphere, Earth would have been below freezing for all times older than 2 billion years ago. The fact that Earth's rocks provide evidence for liquid water since at least 4 Ga requires some combination of enhanced greenhouse effect or lower albedo on the early Earth. Figure modified from Kasting et al. 1988, *Sci. Amer.* 256:90–97.

Calculation of early Earth's blackbody temperature for a sun with 70% of its present luminosity leads to a baseline (blackbody) temperature of only –26°C. If Earth's albedo were the same as it is today, the temperature absent a greenhouse effect would have been a frigid –47°C, similar to Mars's temperature today! With a greenhouse similar to today, temperatures on Earth would still have been below freezing. This conflicts with evidence for abundant liquid water throughout Earth's history. This conflict, referred to as the *faint young sun paradox*, can be resolved either by having substantially less reflective cooling with an albedo more akin to Mercury or the moon, or a much enhanced greenhouse effect that could provide some 55°C of greenhouse warming. This enhanced warming would require higher concentrations of greenhouse gases. Proposals include much higher CO_2 contents or an atmosphere with significant methane, which would be possible in an atmosphere with no O_2.

Even more notable is that Earth's surface temperature has stayed in a narrow range over billions of years of progressive change in solar luminosity (Fig. 9-9). As the sun's luminosity increased over time, Earth's atmosphere precisely accommodated to maintain a stable surface temperature. This fact suggests a sensitive feedback mechanism, a kind of terrestrial thermostat that is able to maintain a constant surface temperature in the face of changes in external forcing. What could be the detailed mechanisms leading to such stability? Why has this mechanism not acted on other planets?

Earth's Long-Term Thermostat

Despite changes in solar luminosity, moving continents, periods of ice ages when glaciers covered much of the globe, warm periods when reptiles thrived at the poles, vast changes in life, and the amount of O_2 in the atmosphere, Earth's temperature appears to have remained comfortably within the range of 0° to 100°C for most of geologic time. We now explore the likely mechanism that has permitted this steady-state condition in the face of large changes in conditions.

Carbon dioxide plays an extremely important role in establishing a planet's surface temperature. In Earth's atmosphere CO_2 is second only to water in its greenhouse capacity. Nonetheless the amount of carbon in the atmosphere is trivial compared to the vast quantity of carbon at the surface. Most of this carbon resides in sediments, part as calcium carbonate (called *limestone* by geologists) and part as organic residues (called *kerogen* by geologists). Fortunately, only a tiny fraction (about sixty atoms out of every million) is currently in the atmosphere as CO_2. Were all Earth's carbon in the form of gaseous CO_2, its amount would exceed that of N_2 and O_2 by a factor of about 100. The pressure exerted by this CO_2 atmosphere would be a staggering 100 atmospheres (similar to the pressure experienced by the hull of a nuclear submarine submerged to a depth of 1 km). Since CO_2 plays such a central role in greenhouse warming, the partitioning between solid $CaCO_3$ and gaseous CO_2 must play a key role in climate stability.

A very interesting argument can be constructed to show how Earth's climate may have been maintained in conditions where liquid water is

stable by a carbon cycle involving atmospheric CO_2 and $CaCO_3$. The long-term climate thermostat has to do with the connections between solid Earth geochemical cycles, weathering, composition of the atmosphere, and seawater composition. Climate control is not just the weather!

As rain falls on rocks and soils, there are chemical reactions that lead to weathering and release of chemicals. River water then carries these elements to the oceans. The Fe is immediately precipitated; the Mg and much of the Na are taken up by the ocean crust. Al is kept in clay minerals and is relatively inert. This leaves Ca and Si as important elements. Not surprisingly, both these elements are deeply involved in modern biogeochemical cycles and make up the shells of diverse organisms that form in the ocean and whose precipitation leads to cherts (in the case of SiO_2) and carbonates (in the case of $CaCO_3$). Most of the Ca and Si come from the breakdown of feldspars, pyroxenes, and other mafic minerals that are common in the continental crust. Because the major players in the climate context are Ca and Si, we can simplify the discussion to breakdown of the Ca-silicate component using the mineral wollastonite, with the formula $CaSiO_3$. This mineral is broken down by interaction with water and CO_2 dissolved in soils to form dissolved ions calcium, bicarbonate, and neutral silicate:

$$3\,H_2O + 2\,CO_2 + CaSiO_3 \rightarrow Ca^{2+} + 2HCO_3^- + H_4SiO_4^0$$
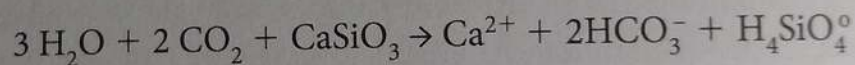
These ions percolate through the soil to a nearby stream and eventually to the sea. In the modern ocean, organisms use these constituents to manufacture their shells. Prior to the evolution of shell-forming organisms, calcium carbonate could precipitate directly from seawater inorganically. In both cases the reaction can be written as:

$$Ca^{2+} + 2\,HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2$$
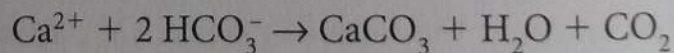
Silica can also be precipitated as opal by the reaction:

$$H_4SiO_4^0 \rightarrow SiO_2 + 2\,H_2O$$
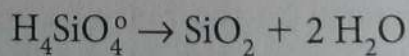
The calcite ($CaCO_3$) and opal (SiO_2) hard parts fall to the seafloor to contribute to the sediment that accumulates on the oceanic plates as they move to the convergent margin where it is subducted. As will be

described in Chapter 12, the high temperatures and pressures of the interior cause the minerals to break down in a process called *metamorphism*. Restricting ourselves to the Ca and Si components of those reactions, the calcite reacts with the opal to yield wollastonite and carbon dioxide gas:

$$SiO_2 + CaCO_3 \rightarrow CaSiO_3 + CO_2$$
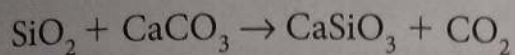
The calcium silicate is returned to the mantle, compensated by the Ca and Si that are included in the magmas rising to the surface from melting of the mantle. The CO_2 dissolves in the magma that rises to the surface, where the solubility of CO_2 is so low that it is released out the convergent margin volcano to the atmosphere (Fig. 9-10).
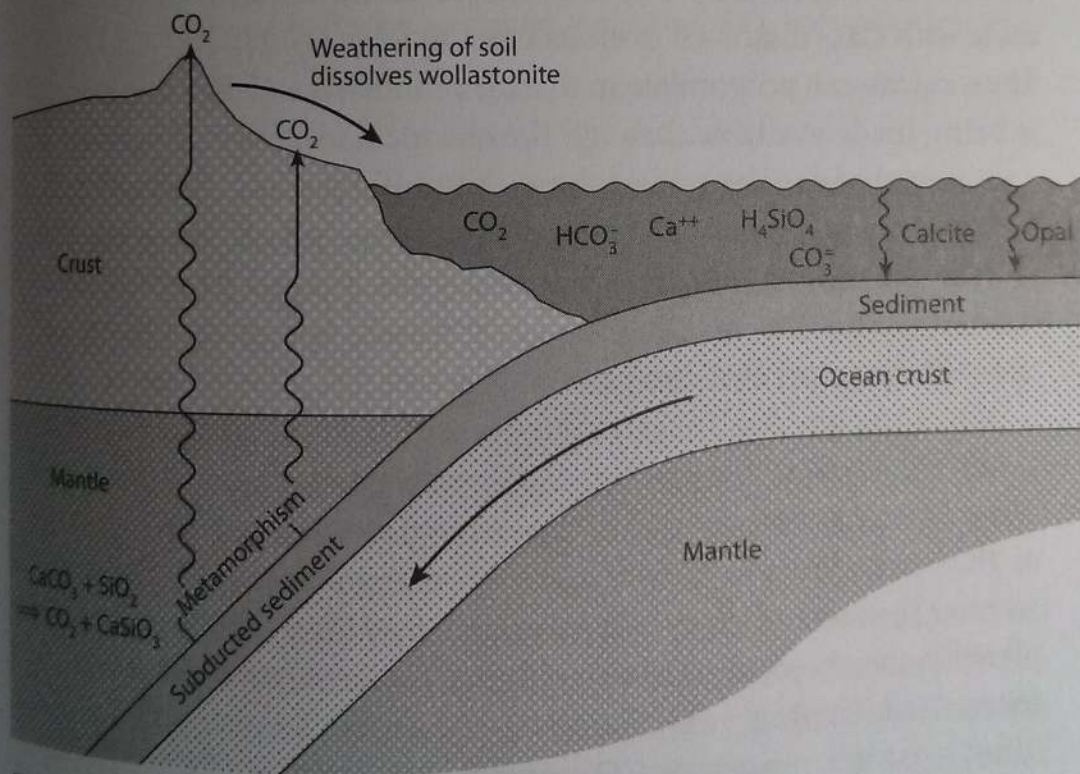

Fig. 9-10: The subduction of oceanic crust beneath the continents carries part of the blanket of sediment deep into Earth's mantle: Here they are heated and metamorphosed. During this process, some of the carbonate minerals contained in the sediment are broken down, releasing CO_2. This CO_2 migrates back to Earth's surface and rejoins the ocean-atmosphere reservoir. Eventually it recombines with calcium in the mineral calcite. This calcite is buried on the seafloor and starts another trip toward a subduction zone.

So much for the background. The interesting aspect of this cycle is how it interacts with the CO_2 content of the atmosphere. The basic driving mechanism for the cycle is the plate motions that carry sediment from Earth's surface to the interior, releasing CO_2 gas. Along with the amount of carbonate sediment on the down-going plate, this sets the rate at which CO_2 is returned to the atmosphere-ocean system. If at any given time CO_2 is not removed from the ocean through calcite burial in the sediments as rapidly as it is added to the atmosphere-ocean reservoir, then the CO_2 content of the atmosphere would steadily increase. If, on the other hand, organisms were to remove calcite from the ocean too rapidly, the CO_2 content of the ocean-atmosphere system would steadily decline. Somehow a balance between the supply of CO_2 to the ocean-atmosphere reservoir and removal of CO_2 must be achieved. Key to this balance is the requirement that in order to form calcite, organisms need calcium as well as CO_2. The CO_2 that leaks from Earth's interior must mate with CaO dissolved from its crust to form $CaO\ CO_2$ (i.e., $CaCO_3$). Thus, calcite can accumulate in marine sediments no faster than calcium is being made available through the chemical reactions taking place in continental soils. The rate of these chemical reactions depends on the temperature of the soil (all chemical reactions go faster when the reactants are heated), the acidity of the water (which causes minerals to break down more rapidly, and the rainfall (the more water that runs through the soils, the more that can be carried away).

Now come the feedbacks to this cycle of events (Fig. 9-11). As stated above, if CO_2 were to be added to the atmosphere faster than it was removed by calcite deposited in deep-sea sediments, then the CO_2 content of the atmosphere would increase. This would make the planet even warmer (because of the increased greenhouse blanketing) and make the planet even wetter (warmer air holds more water vapor and hence makes more rain). The higher CO_2 content also makes the water more acidic. Thus, a rise in atmospheric CO_2 content would increase the rate at which calcium dissolves from the continents and thereby permit calcite to accumulate more rapidly in marine sediment. Eventually the calcite production rate would become great enough that CO_2 could be removed from the atmosphere-ocean system as fast as it was added. The CO_2 buildup would be stemmed.
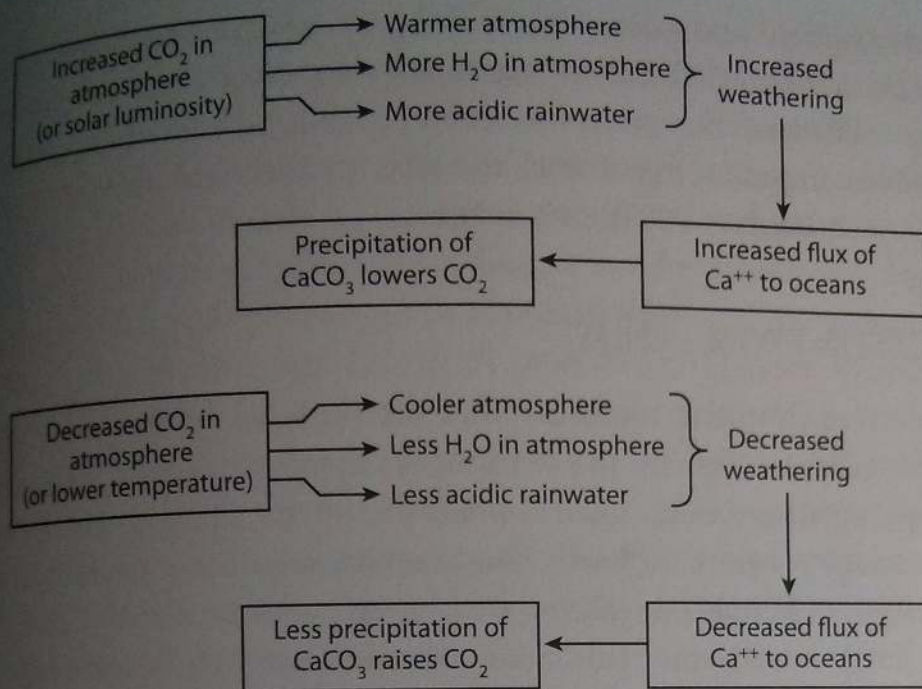
Fig. 9-11: Illustration of feedbacks that control atmospheric CO_2 and surface temperature on Earth, as described in the text.

The feedback also works in the other direction. If for any reason temperature in the atmosphere gets particularly low, weathering will slow, diminishing Ca supplies and carbonate precipitation, causing CO_2 to rise. Or if CO_2 becomes too low in the atmosphere, temperature, rainfall and acidity will decline, limiting CO_2 removal from the system by cutting off the supply of Ca. This process requires long periods of time to take place, because weathering, sediment precipitation, and subduction are slow processes. It is Earth's *tectonic thermostat*, operating on tectonic timescales of $>10^5$–10^7 years.

The hypothesis of a tectonic thermostat has great appeal because some strong feedback mechanism is necessary to preserve climate stability over billions of years of planetary history where the radiation from the sun has changed substantially and where events such as great volcanic outpourings, meteorite impacts, or "snowball Earth" episodes (discussed below) might lead to catastrophic long-term effects. This hypothesis lacks direct tests, however. Quantitative estimates of the changes in weathering rates with atmospheric CO_2 are hard to come by, the fate of carbonates during subduction is a subject of debate, the chemical compositions

of atmosphere and oceans have changed over Earth's history in ways that are not well defined, and thermal evolution of Earth's interior may have influenced metamorphic reactions in subducting plates. Absent a viable competing hypothesis, the idea is widely accepted, but on our scale of certainty it still merits only a 6.

A LESSON FROM VENUS

We have a dramatic reminder that the situation with regard to CO_2 could well be different. The reminder is the planet Venus, which has a whopping atmosphere made almost entirely of CO_2, with ninety times the surface pressure on Earth. The greenhouse effect of this CO_2 atmosphere gives Venus the scalding surface temperature of 464°C. As Venus and Earth have nearly the same size and nearly the same density, it seems reasonable that they also started with a similar inventory of volatiles. Indeed, the fact that the amount of carbon in the CO_2 of the Venusian atmosphere is about the same as the amount of carbon locked up in limestone and kerogen on Earth's surface provides evidence that this is true.[1] Thus, Venus has the conditions that would prevail on Earth if all the CO_2 locked up in limestone and kerogen were to be released as CO_2 to the atmosphere.

However, when comparing Earth and Venus, a problem arises in connection with water. If Venus started with the same component of volatiles as Earth, it should have a sizable ocean (or rather, at its high temperature, an atmosphere dominated by steam).[2] Not only is the atmosphere of Venus not dominated by steam; water vapor is barely detectable.

Most scientists believe that the hydrogen initially present on Venus as water escaped to space. In the very hot Venusian atmosphere, water vapor would be effectively transported to the "top." Here it could be dissociated by ultraviolet light to form hydrogen atoms that would then escape. The "left behind" oxygen atoms would be stirred back down through the atmosphere to the surface of the planet, where they would

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[1] Because Venus is so hot, it surely has no life and hence no kerogen. Also, $CaCO_3$ would decompose under these conditions, releasing its carbon as CO_2 gas. Hence, it is likely that nearly all carbon on the Venusian surface resides as CO_2 gas in its atmosphere.

[2] If the Earth were heated to the point where its ocean was converted entirely into steam, this steam would exert a pressure about 270 times that of the present Earth atmosphere.

gradually convert the FeO in the hot Venusian crust to Fe_2O_3. Evidence in support of this hypothesis was obtained when an unmanned American space probe was dropped into the atmosphere of Venus. Before this probe was rendered inoperative by the high temperatures, it measured and radioed back to Earth the isotopic composition of the trace amount of water present in the Venusian atmosphere. The astounding finding was that the amount of deuterium (^2H) relative to ^1H in Venusian water is >100 times higher than the $^2H/^1H$ ratio in Earth water. Because of their twofold larger mass, deuterium atoms have a much lower escape probability than do hydrogen atoms. Hence, the escape of hydrogen from Venus would tend to enrich the residual water in deuterium. While the observed hundredfold enrichment of deuterium does not prove that Venus once had as much water as Earth, it can only be explained if Venus once had at least a thousand times more water than it does now!

Thus, it is entirely possible that Venus and Earth started with roughly the same volatile ingredients. Earth for some reason evolved along a path that kept its carbon safely locked up in sediments and hence avoided the disastrous consequences of a so-called runaway greenhouse warming. Venus, on the other hand, at some point slipped and let CO_2 build up in its atmosphere. This buildup led to high temperatures, which would have terminated life (if indeed it ever achieved a foothold on Venus). It is hard to imagine how a planet once in this very hot state could ever cool off.

We have little knowledge of the history of Venus. It is difficult to imagine that astronauts will ever roam about its surface as they did on the moon. While the Russians and Americans have managed to land several unmanned space probes on the hot surface of Venus, these vehicles survived the hostile conditions only long enough to radio back information about the temperature, pressure, and composition of the Venusian atmosphere and (as we learned in Chapter 4) about the potassium to uranium ratio in the rock surface upon which the probe landed. Radar beams bounced off Venus tell us that its surface has large topographic features and a young surface lacking in large-impact craters. Because of the young surface, we do not know whether Venus might have had an earlier history more like Earth's. Certainly in the early solar system with the luminosity of the sun 30% less than present, Venus would seem to have been in a favorable position for life within the solar system.

In any case, after the runaway greenhouse, conditions permitting the development of life were never reestablished. We can speculate that Venus's runaway climate occurred because Venus is closer to the sun than Earth and was not able to manage the increase in solar luminosity. Was it also that Venus spins hundreds of times more slowly than Earth? Was it because life never got started on Venus? Was it because the initial component of water on Venus was much smaller than that on Earth? In any case, Venus's presence reminds us that climate stability is not assured, sending a message that planetary climate can go catastrophically off course.

SNOWBALL EARTH

With this background in mind we can try to envision what would happen if Earth's ocean were to freeze. There would be no marine organisms to make calcite, nor would there be water from which calcite could precipitate inorganically. There would also be no chemical erosion. Under these conditions, the CO_2 released from Earth's hot interior would build up and up in the atmosphere until the temperatures became warm enough to melt the ice. The secret of this escape hatch is that CO_2 outgassing is driven by Earth's internal heat and is therefore insensitive to the surface temperature. A part of Earth's history where such a scenario took place would be a useful test of the tectonic thermostat.

Until very recently it was believed that Earth had never been entirely frozen. But then two Harvard geologists, Paul Hoffman and Dan Schrag, picked up on a suggestion made in 1992 by Caltech's Joseph Kirschvink that during the episodes of glaciations that occurred during the Neoproterozoic period from 580 to 750 million years ago, Earth did indeed become totally frozen. Kirschvink referred to these episodes as *snowball catastrophes*.

The key observation is as follows. Deposits formed at this time by glaciers were intermingled with marine sediment. In other words, the glaciers must have reached sea level. Further, paleomagnetic measurements demonstrate that these deposits were widespread over a range in latitude. More important, some of these glaciers were located near the equator at sea level, giving rise to the possibility that the entire Earth was frozen. Such a state could arise more easily if oceans covered the
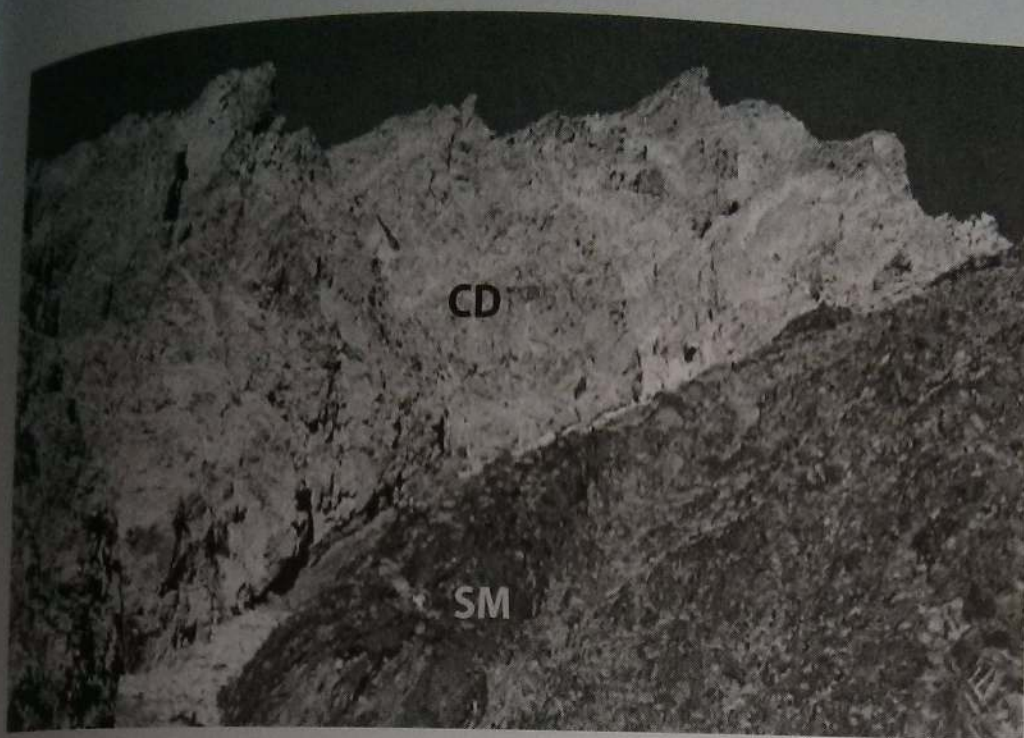
Fig. 9-12: The Noonday cap carbonate (labeled CD) lies above the upper Kingston Peak (Surprise Mb) (labeled SM) glacial deposit called a *diamictite*, The outcrop is in the Panamint Range, Death Valley area, California. Height of cliff ~300m (~1,000,ft). Note the abrupt transition between thick glacial deposits, indicating an ice age, and the carbonate sequence that indicates warm conditions. (Courtesy of Paul Hoffman; www.snowballearth.org)

poles, since growth of oceanic ice cover is far easier than growth of continental ice sheets. If polar ice begins to grow, it increases Earth's albedo, causing more light to be reflected back into space. If the ice passes a critical surface area, then the albedo lowers the atmospheric temperature, and there is a positive feedback leading to more sea ice that can extend all the way to equatorial latitudes.

Key to the thinking of Hoffman and Schrag was the observation that these glacial deposits are overlain by thick sequences of calcium carbonate (Fig. 9-12). Carbonates are generally deposited in warm seas, so explaining why they would occur immediately above a glacial deposit was quite a puzzle. These so-called *cap carbonates* have textures unlike any other limestone in the geologic record. Not only are their textures different but so also is the isotopic composition of their carbon. Its composition lies well away from that of "normal" limestones and instead closely matches that of average Earth carbon.

Hoffman and Schrag created a scenario based on the tectonic thermostat that is an intriguing hypothesis to explain these observations. After the ocean froze over and continental glaciers descended to the shores of the sea, chemical erosion ceased. No more Ca was delivered to the oceans by rivers (some would still be delivered by hydrothermal vents), and the deposition of calcium carbonate and organic residues would drastically decrease. Plate tectonics continued to operate, however, so CO_2 continued to escape from the interior through volcanoes that would melt their way through the ice. As no mechanism existed for the removal of this CO_2, its concentration in the ocean and atmosphere went up and up. As it rose, Earth gradually warmed despite the very high albedo of the 100% ice cover. After 10 or so million years, the CO_2 greenhouse effect was large enough that the ice began to melt. The melting led to a runaway warming, for as the highly reflective ice and snow was replaced by far less reflective sea and land, less sunlight would be reflected, leading to a positive feedback toward increased melting. Erosion would then have reinitiated with a vengeance, supplying calcium to the CO_2-rich ocean. This, of course, led to the precipitation of massive calcium carbonate deposits. As the CO_2 was used up, our planet's surface cooled down towards more normal temperatures.

Sun Protection

One final ingredient is needed to make the planetary surface conducive to the origin and long-term evolution of life. The sun emits both ultraviolet radiation and a solar wind of charged particles with very high velocities. Particularly for early Earth, the solar wind could have contributed to stripping of the early atmosphere and possibly led to loss of the volatiles that are critical for climate stability and life. At the same time, galactic cosmic rays coming from distant stars also have the potential to deliver doses of radiation detrimental to life. Once life began, this radiation would have created a high dose of radioactivity that would have been hazardous to life as we know it. While the sun is the ultimate source of habitability, some protection against cosmic radiation is necessary.
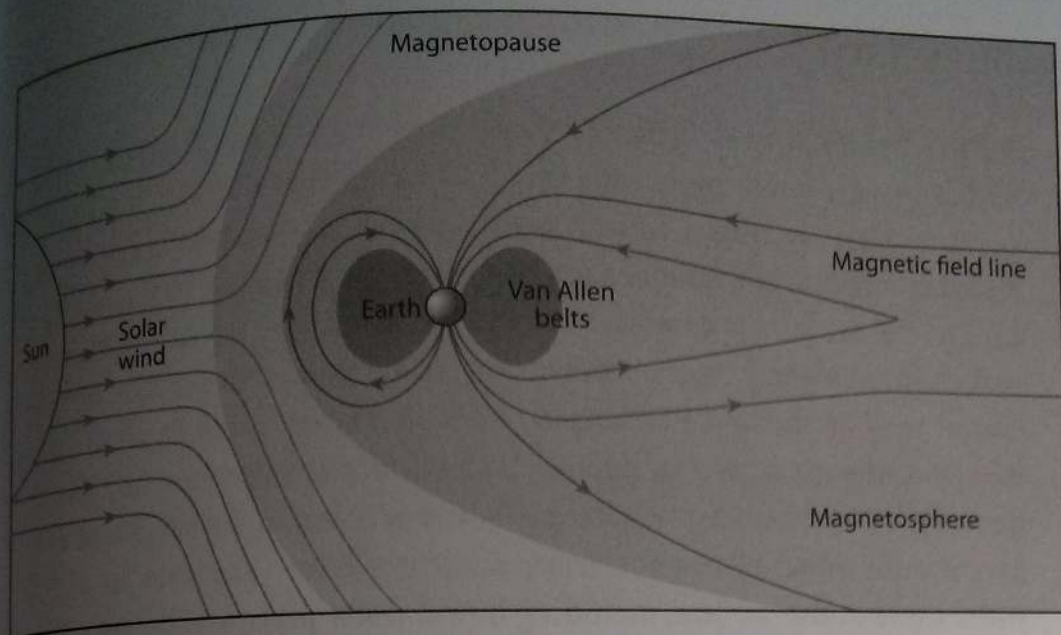
Fig. 9-13: Graphical illustration of the protection from the Sun's solar wind provided by Earth's magnetic field. The solar wind is deflected away from Earth, providing protection for the atmosphere and surface.

Earth's sun protection is its atmosphere and magnetic field. In the modern atmosphere ozone absorbs much of the Sun's ultraviolet radiation, protecting life on land from its effects. It may be no accident that macroscopic life was able to evolve and take over the continental surface only after there was sufficient oxygen in the atmosphere to give rise to an effective ozone shield.

For cosmic rays and the solar wind, the principal protection is Earth's magnetic field. We are all familiar with Earth's magnetic field through compasses and their importance for navigation. Magnetic fields also exert a force on charged particles such as those in cosmic radiation. Earth's magnetic field causes most of the particle radiation from the sun to be diverted around the planet (Fig. 9-13).

Earth has the largest magnetic field of any of the terrestrial planets. The magnetic field is generated by convection in the liquid outer core. Since Earth has been cooling since its early history of accretion, a liquid core would also have been present in the early Earth, and the sun protection provided by the magnetic field likely contributed to early habitability and the possibilities of an origin of life.

Summary

Earth's habitability is critically dependent on a surface environment with adequate volatiles, oceans and continents, liquid water, and a temperature that remains within a restricted range over billions of years. Because Earth as a whole has few volatiles, early concentration of volatiles to the surface is essential to provide an ocean and atmosphere. A sufficient planetary mass, protection from atmospheric loss, and a "water trap" in the lower atmosphere enabled Earth to retain all its volatiles with the exception of helium. The surface temperature of a planet depends on the amount of solar radiation it receives, its albedo, and its greenhouse effect. Evidence from ancient zircons suggests an active water cycle at the surface, including liquid water prior to 4 billion years, and the record of sedimentary rocks shows that water has been present at Earth's surface since that time. It is remarkable that Earth has managed a stable climate over billions of years, despite a 30% change in the solar luminosity. This fact suggests a robust feedback mechanism that would enable greater greenhouse warming in the early Earth. A tectonic thermostat involving the carbon cycle is the most likely mechanism for climate control. A warmer atmosphere with high CO_2 would lead to greater weathering, causing more CO_2 to be sequestered in carbonate rocks. The efficacy of this mechanism is apparent by comparison with Venus, where CO_2 was not sequestered into carbonates, leading to massive greenhouse warming and loss of planetary water, making the planet unsuitable for life. A planetary surface suitable for life is also greatly enhanced by the presence of a magnetic field. Earth's liquid outer core provides the largest magnetic field of any of the terrestrial planets. The magnetic field would have contributed to prevention of atmospheric loss in early Earth's history, and it protects the planet from deadly cosmic rays, providing Earth with billions of years of homegrown sun protection.

Supplementary Readings

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