Atmospheric Evolution of the Terrestrial Planets

Donald M. Hunten

The major atmospheric gases on Earth, Venus, and Mars were probably CO_2, H_2O, and N_2. Most of the Earth's CO_2 is tied up in minerals such as limestone, and Venus has lost most of its H_2O, leaving the CO_2 in the atmosphere. Much of Mars' atmosphere may have been eroded in impacts by large meteoroids early in solar-system history. Noble gases are very underabundant everywhere, and must have been lost during an early period; they were probably dragged along during rapid loss of massive amounts of hydrogen. The tenuous atmospheres of Mercury and the moon have lifetimes of a few days or less and must be continuously replenished from internal or external sources.

The terrestrial planets with substantial atmospheres are Earth, Venus, and Mars. Evolution of the Earth's atmosphere is discussed by Kasting (*1*); I therefore emphasize Venus and Mars, except where comparison with Earth is illuminating. One major reason to be interested in these other atmospheres is that they are not, and probably never have been, influenced by the biological processes that are so important on Earth. Although Mercury and the moon are usually thought to be airless, they do have detectable atmospheres, which I discuss briefly at the end.

The sun, the planets, and their atmospheres are generally believed to have condensed, about 4.6 billion years ago (Ga) from a primitive solar nebula. The nebula is thought to have had the same composition as the sun, mostly hydrogen and helium but with a small sprinkling of heavier elements. Oxides and hydrides of the heavier elements (rocks and ices) must have condensed into particles and accreted to form the planets. The Jovian planets were able to retain a substantial amount of the gas as well, and their satellites and ring systems contain ice as well as rock. The terrestrial planets are mostly rock with a small amount of the icy material, much of which appears in their atmospheres and the Earth's ocean.

The original dust grains must have accreted, by processes still not well understood, into bigger and bigger objects. In simulations by Wetherill (*2*) of the later stages, it is assumed that there were about 500 of these planetesimals, roughly the size of our moon, in the region now occupied by the terrestrial planets, and their merging into planets is modeled. The planets found, although different in each run, have a general resemblance to what we now find in the inner solar system. An important result of these studies is that bodies from anywhere in the inner solar system might end up as part of any of the terrestrial planets. The mechanism is gravitational perturbations, especially by the larger planetary embryos, that increase the eccentricities of the orbits. The consequence is that the initial atmospheric compositions should be similar, and indeed those of Venus and Earth have many interesting resemblances. Mercury and the moon appear to have lost all or most of their original gas, or were unable to retain any in the first place. If Venus originally had as much water (vapor or liquid) as the Earth, nearly all of it must have been lost, and this loss was facilitated by the likely existence of a runaway greenhouse effect early in its planetary history, fed by the vaporization of water, which then becomes readily available to be dissociated and lost.

This scenario is not universally accepted. Another school (*3*) attributes the differences among the planets to differences in their distances from the sun, and the consequent effect on their initial compositions. Supporting this idea is the observed gradient of mean density from Mars to Mercury, which demonstrates that the planets do not have uniform bulk composition: according to this model Mercury accreted from dry, rocky material, Venus retained some form of carbon, but water was accreted only on Earth and Mars.

The author is in the Lunar and Planetary Laboratory, The University of Arizona, Tucson, AZ 85721.

Present and Initial Compositions

Mars' atmosphere, like that of Venus (Table 1), is mostly CO_2, a gas that on Earth mainly resides in the crust as carbonates (*4–6*). There are probably large additional quantities of both CO_2 and H_2O in the polar caps, as well as the soil: ice is stable in the subsurface at high latitudes, and carbonate rocks may be abundant. Parts of Mars show clear evidence of formerly abundant running water, but liquid water, under present conditions, will either freeze or flash into vapor. The vaporization would be inhibited by a modest increase of surface pressure, but the surface temperature would still be too low for liquid water. Some greenhouse calculations suggest that a CO_2 pressure of about 1 bar would raise the temperature above the freezing point. However, in recent work, Kasting (6) found that the temperature was not high enough if the solar flux is reduced by 30% from the present value, as it probably was in the early solar system. Possible remedies are additional solar heating of suspended dust (certainly important today), or a modified solar model, such as the one discussed below. The original amount of H_2O (0.5 to 1 km, equivalent of 30 bars) has been estimated from geological evidence (8), for example the size and number of former stream beds. Considerable extrapolation is involved, and the estimates shown in Table 1 are uncertain upper limits. Other studies, stressing evidence from the high D/H ratio in the atmosphere, suggest that there are considerably smaller amounts of H_2O and CO_2, unless the reservoirs are completely isolated from the atmosphere (9).

The noble gases are significant for understanding of atmospheric evolution because of the large number of isotopes, the wide range of mass, and because we can be reasonably sure that the entire inventory resides in the atmosphere. The exception is He, which was omitted from Table 1 because it escapes, at least from Earth and Mars, in times short compared with the age of the solar system. Noble gases cannot be measured remotely; the data base relies on mass spectroscopy from probes and landers, supplemented for Mars by analysis of the

Table 1. Atmospheric compositions of Venus, Earth, and Mars (in parts per million by volume except for CO_2 and N_2 or as indicated). In addition, the Earth's oceans contain the equivalent of 270 bars of H_2O and the crust 53 bars of CO_2 and C. Estimates for Mars are 30 bars of H_2O and 20 bars of CO_2 and C.

Planet	Total (bars)	CO_2 (%)	N_2 (%)	He	Ne	Ar	^{36}Ar	Kr	Xe	H_2O	D/H
Venus (*4*)	92	96.5	3.5	~12	7	70	35	0.05	<0.04	30 to 200	0.022
Earth (*5*)	1.013	0.033	78	5.2	18.2	9340	31	1.14	0.087	≤3%	1.5×10^{-4}
Mars (*6*)	0.006	95.3	2.7	<100	2.5	16000	5	0.3	0.08	≤100	9×10^{-4}

rare SNC meteorites, which are widely believed to be from that planet and to have preserved a sample of its atmosphere. The concentrations of noble gases are deficient relative to solar abundance on Earth, Mars, and Venus by factors between 1×10^6 and 1×10^{13} (Fig. 1).

The D/H ratio is strikingly enriched in Venus' atmosphere relative to the value in the Earth's oceans (the factor is ~150), and substantially in Mars' atmosphere. The Earth value itself (as well as that of Comet Halley and many meteorites) is enriched by a factor of 10 relative to the cosmic ratio, 1.65×10^{-5} (*11*). If Halley is representative of the raw material for planetary water, no additional enrichment occurred on these planets; it is also possible that we are seeing the consequences of some selective escape process that is more efficient for H than for D.

The $^{15}N/^{14}N$ ratio on Mars is enriched by a factor of 1.62 compared with that for Earth (not shown in Fig. 1 or Table 1). Again, the probable explanation is selective escape, favoring the lighter isotope, over the age of the planet.

If the original D/H ratio for all the planets was cosmic, the current deuterium enrichments are a factor of 10 for Earth, 60 for Mars, and 1500 for Venus. If the planets accreted from enriched material such as that in comets (currently the more popular hypothesis), these numbers are smaller by a factor ~10. In either case, there must have been selective escape from at least Mars and Venus. An enrichment by a factor of x requires that the original amount of H was at least x times the present amount; in the likely case that some of the D has also been lost, these factors become even larger. If there was a rapid blowoff phase, as discussed in the next section, even more H would be required, because this process is not efficient at enriching D. Thus, it is likely that even Earth has lost a considerable amount of H.

The extreme enrichment of D on Venus certainly points to loss of almost all the original H. However, it is impossible to work back to the actual amount with any assurance, because of the complicating factors mentioned above and because even the present amount is still uncertain. It is even possible (*12*) that the current inventory is not primordial at all but is in steady state with input from the occasional comet. However, this extreme view is not widely held, and the most popular one is that we see the remnant of a much larger endowment, quite possibly an amount equivalent to the Earth's ocean.

The accretion of carbon presents a different puzzle, because no simple common C compounds (CO_2, CO, and CH_4) form ices at the temperatures thought to have existed in the inner solar system during accretion. The hydrocarbons, another common class of molecule, are much more likely to condense. Although equilibrium thermochemical models of the composition of the solar nebular gas do not yield such heavier hydrocarbons, they are common in nature, even in an abundant class of primitive meteorites, the carbonaceous chondrites, and many nonequilibrium paths to their formation are known. Carbon might also be accreted in forms such as graphite and organic compounds containing O and N as well as C and H, the simplest example being formaldehyde H_2CO.

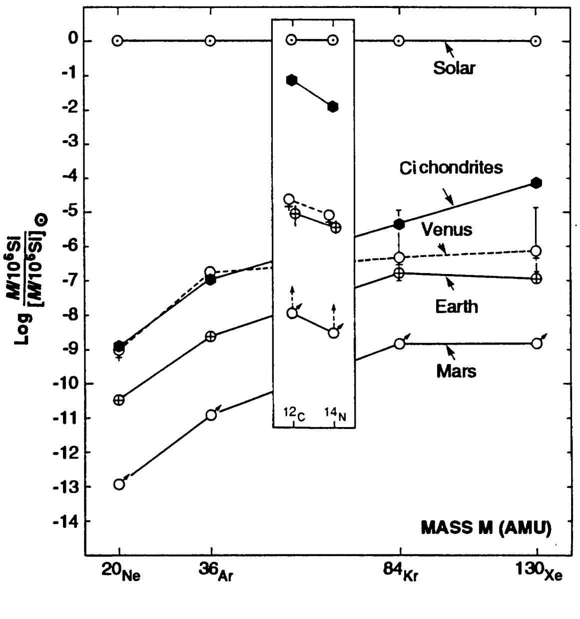

Fig. 1. Abundances of noble gases, C, and Ni in the atmospheres of Venus, Earth, and Mars and in CI meteorites (a type of carbonaceous chondrite), with respect to solar ratios. Units are atoms per 10^6 planetary Si atoms. For C and N on Earth, crustal reservoirs are included. [Modified from (*10*)]

At the high temperatures and pressures likely to have existed during rapid accretion, hydrocarbons and water can react to produce CO_2 and H. Because H is likely to escape, the system is driven in this direction, and six H atoms or three H_2 molecules are produced for each CO_2 molecule formed. This is an attractive path to the production of CO_2 and of the H needed to drive a hydrodynamic escape flow.

Evolutionary Processes

Thermal escape. The classic example of an escape process for light gases is thermal or Jeans escape, formulated in 1904 (*13, 14*). The basic idea is that, above some critical level now usually called the "exobase," atoms in the high-velocity tail of the Maxwellian distribution must escape if they are directed upward at or above the escape velocity, which is 11.2 km/s for Earth. The exobase level is 500 to 600 km for Earth. Thermal escape generally explains the observation that only the most massive bodies in the solar system have dense atmospheres, and also that atmospheres are generally deficient in light atoms such as H and He (except in the Jovian planets). It does suggest that heavy gases, and possibly even N, should be stable on our moon, and at the beginning of this century the lack of a substantial lunar atmosphere was a stumbling block to the acceptance of the Jeans equation. Of course, the objection vanishes if the moon never had such an atmosphere. Other loss processes probably dominate, at least currently.

When examined in more detail, thermal escape is found to be unattractive as a mechanism for substantial evolution of an atmosphere. First, because the escape is from a level with a low density, the actual quantity of gas that can be processed is rather small by planetary standards. One remedy that has been explored is to assume that the escape took place from a multitude of planetesimal-sized bodies before they accreted into planets (*15*). Second, the principal term in the Jeans equation is $e^{-GMm/kTr}$, where G is Newton's gravitational constant; M, r, and T are the planetary mass and the radius and temperature of the exobase; m is the atomic mass; and k is Boltzmann's constant. The noble gases from Ne to Xe cover a mass range of more than 6 to 1; if Xe escapes at all, Ne would be gone in a flash. Figure 1 shows a trend in the right direction, with lighter elements more depleted than heavier ones, but the trend is not nearly as large as the exponential term would predict.

Blowoff and solar evolution. A much more recent idea is that a rapid hydrodynamic outflow (or blowoff) of a light gas can carry along heavier gases at a rate that has a linear dependence on mass, rather than the exponential one of the Jeans equation (*16*). Likely gases are H or H_2, or possibly even CH_4. Substantial quantities of gas can be processed. The mechanism for loss of heavier atoms is essentially aerodynamic drag, although it is formulated in terms of a two-component diffusion equation. Because all noble gas atoms have nearly the same diameter, they all experience nearly the same upward drag. But they also experience a downward force (their own weight), and the net force is strongly mass-dependent. Indeed, for the heavier atoms the drag force can be smaller than the weight; there is thus a crossover mass (dependent on the light-gas flux) above which there is no escape, although the heavier gases take on an abnormally large scale height.

Although this theory is straightforward, the importance of the process depends on whether the necessary driver flow ever existed. The H must come from accreted gas or from water vapor, which can be photodissociated or react with hydrocarbons or crustal iron. The solar heat to run the flow must be deposited high in the atmosphere. The relevant wavelengths are the ionizing ones less than ~100 nm, which contain ~1×10^{-5} of the present solar spectral power. To drive a suitable flow of H_2 from Earth or Venus would require ~100 times as much short-wavelength radiation, decaying over a period of a few hundred million years. This requirement is in excellent agreement with ultraviolet excesses observed in T Tauri stars, which are believed to be young stars similar to the sun at the appropriate period. One residual concern is that the radiation might be absorbed by the gas of the solar nebula before it reaches the planets. Evidently such absorption is not affecting the observed T Tauri stars, because the wavelengths in question do reach the Earth, but one cannot be sure that the same was true in the early solar system. Another concern is the requirement for huge quantities of H to drive the process.

Another aspect of solar evolution is that theories of the sun's interior predict that its total output increased by 30% over the past 4.6×10^9 years (*17*). Thus, Venus may originally have had a liquid ocean which later evaporated and was lost. Geological evidence that both Earth and Mars were as warm as today, or even warmer, has prompted the suggestion of strong greenhouse warmings to offset the reduced solar input. Alternatively, in order to explain the depletion of lithium in the solar atmosphere (*18*), it has been postulated that the sun started with about 10% more mass than it now has and lost this excess by some unknown process. As a corollary, the solar flux at the planets would have started out 30% greater than it is today. The duration of the mass loss is unconstrained; if it was 1 or 2 billion years, the excess flux would have decayed over the same period, and the minimum flux would be 85% of the present value. These ideas are still untested.

Impact erosion. The impact of a planetesimal can erode part of the existing atmosphere or add volatiles to it. The balance depends on the composition of the impactor and on the mass of the growing planet. Once Earth and Venus had attained nearly their present masses and escape velocities, erosion became very inefficient, but Mars was rather vulnerable (*19*), and still would be if the population of impactors had not essentially died out. The currently reigning theory of the moon's origin holds that it is the result of the impact of a Mars-sized body with the proto-Earth; among many other things, this hypothesis neatly accounts for the extreme lack of volatiles on the moon. It is also speculated that the Earth itself would have lost all the atmosphere it had at the time, but quantitative models are lacking. Mercury also may have been completely disrupted by a large, late collision (*20*); most of the fragments (but not the volatiles) would have then reaccreted, because all their orbits shared a common point. Such an event would account for the high mean density of the planet, without requiring it to have been generated during accretion.

Once an atmosphere had been eroded, it could have been resupplied by further accretion of comets. Owen *et al.* (*21*) have proposed a model of this sort, in which noble gases are absorbed in cometary material formed at about 50 K. It is not clear, however, that this process can explain the isotopic structures observed.

Runaway greenhouse. According to current ideas of accretion, Venus should have originally had an amount of H_2O similar to that now on Earth, often referred to as an "ocean" although it may not have been in liquid form. Because Venus receives about twice as much solar heat as the Earth, the humidity of its atmosphere would have been correspondingly greater, and so would the greenhouse warming. There is a critical value of the solar flux above which the ocean evaporates completely into the atmosphere, because there is a positive feedback between the enhanced humidity and the greenhouse warming of the surface. This situation is called a "runaway greenhouse" (*22*). The idea is made all the more plausible because today Venus exhibits a huge greenhouse warming, which generates a surface temperature of 750 K and is sustained by CO_2 with help from some minor constituents (including a remaining trace of H_2O). Evaporation of Earth's ocean would give an atmosphere containing 270 bars of steam. Water molecules in such an atmosphere would be rapidly photolyzed into H and O, and the H would rapidly escape accompanied by a much smaller escape of deuterium. If there was once enough H_2O, there is little doubt that a runaway would have occurred on Venus, although it could have been delayed until the total solar output had risen somewhat from its initial low value.

Crustal and biological interactions. The atmosphere, oceans, and crust interact strongly on Earth at present, and the interaction is strongly influenced by living organisms. Processes include evaporation, precipitation, erosion, subduction, volcanism, fumarolic activity, photosynthesis, metabolism, decay, and combustion. On Mars far more volatiles are probably segregated in or on the crust than in the atmosphere. The hot surface of Venus presumably keeps everything in the atmosphere but also facilitates chemical reactions; for example, if large amounts of H have escaped, the corresponding O must have reacted, probably with minerals containing iron or ferrous oxide.

Nonthermal loss. All the processes discussed so far involve neutral molecules and atoms in a Maxwellian energy distribution, generally called "thermal." The upper parts of an atmosphere (and the entire atmospheres of Mercury and the moon) are partially ionized, by the agency of solar photons with wavelengths generally below 100 nm. These ions are often suprathermal, and their interactions can produce suprathermal neutral atoms as well [the word "nonthermal" is often used]. At the moon, ions are swept away, or precipitated to the surface as soon as they are produced, by the solar wind. Elsewhere, their motions are controlled by local magnetic fields, and they tend to be confined near their point of production, except in special regions such as those near the Earth's poles where the field lines are open (connected to interplanetary space). A substantial outflow of protons, the polar wind, occurs here. A number of processes are important in transferring energy to neutral atoms (*14*, *23*); two prominent ones are charge exchange and dissociative recombination. An example of charge exchange is transfer of an electron between a proton and a neutral H atom to exchange identities but not (in most cases) the energies. Thus, a hot proton is converted to a hot H atom. In dissociative recombination, an electron and a molecular ion, for example N_2^+ or O_2^+, produce two fast atoms. Because gravitational separation enriches the upper parts of an atmosphere in lighter isotopes, both processes indirectly favor their escape, even though the velocities are not strongly dependent on mass. As for thermal escape, these suprathermal processes are limited to modest quantities of gas; nevertheless, they can be important for minor constituents, such as N and O at Mars and H at Venus and Earth.

Another process involving ions pertains to Venus and Mars, which lack a significant intrinsic magnetic field (*24*). These planets possess a boundary, the ionopause, that separates the bound ionosphere from an outer region in which the solar wind is diverted and flows around and past the planet. This region still contains some neutral gas, and if such atoms are ionized by solar photons or electron impact, they are swept up in the flow. Some of these ions can reimpact the upper atmosphere with enough energy to remove additional atoms. Study of this field is still in its infancy, but there are suggestions that the process is significant for loss of O from both Mars and Venus.

Diffusion limit. Under certain circumstances, the escape flux of a light, minor element is limited by the rate at which it can diffuse through the upper atmosphere (*13, 14, 25*). Hydrogen on Earth is an excellent example. Its mole fraction in the stratosphere and above (~13 ppm) is mostly controlled by the cold trap at the tropopause, which causes ice particles to precipitate. The H must diffuse through the lower thermosphere (just above 100 km), and the flux cannot be greater than the value obtained by the assumption that the partial pressure at the top of the atmosphere is zero. The actual pressure is not quite zero, and the actual flux is slightly less than the diffusion-limited value.

Early Evolution

We have little surviving evidence of how atmospheres may have evolved during the early period when accretion was ongoing. Many of the impacting bodies probably had a substantial content of frozen volatiles and occluded gases. They might have been deeply buried, for large objects, or released directly to the atmosphere, for smaller ones. Buried volatiles were degassed, except for a remnant, some of which is still appearing. If the accretion rate and the volatile content were large, the released heat could have been confined by the greenhouse effect to the extent that the surface rocks actually melted (*26*). Large impacts have the potential of eroding part of the atmosphere, and the competition between accretion and erosion can lead to a steady-state atmosphere (*26*). Erosion is unimportant for bodies as large as Earth and Venus, but may have been important on Mars. A Mars model (*19*), based on the best estimates of the meteoroid flux in the early solar system, shows that the entire atmosphere should have been stripped away. If the impactors had been assumed in this study to contain volatiles, it presumably would have found a steady, finite atmosphere.

Blowoff and mass fractionation of noble gases and their isotopes probably occurred in the same early period when, as mentioned above, the ultraviolet output of the sun was greatly enhanced. These processes have been discussed in great detail by Pepin (*10*) for Venus, Earth, Mars, and the parent body of the carbonaceous chondrites (presumably a large asteroid that has since been disrupted). In one scenario (Table 2), blowoff started 50 million years after the sun finished contracting into a stable state; at this start time the nebular gas is assumed to have been cleared out so that the solar extreme ultraviolet radiation could reach the planets. The numerical value of the blowoff rate, and the crossover mass above which there is no escape, are proportional to the solar flux at the object and inversely proportional to its mass and the cube of its radius. Thus, as the solar output falls, the loss of the heavier gases cuts off at a different time for each planet. After blowoff had proceeded for 97 million years, Earth outgassed a fresh supply of noble gases, having an elemental composition characteristic of absorption in nebular grains; 200 million years later the same thing happened on Mars. At 205 million years, Venus and Earth received a veneer of material containing C and N, resembling E [enstatite] chondrites. The finish times, when the solar output fell below the threshold, occur after a few hundred million years (Table 2).

Table 2. Times of various events in Model II of Pepin (*10*) for the blowoff fractionation of noble gases in the atmospheres of Venus, Earth, and Mars. All times in millions of years from the time the sun reached the main sequence. The last line shows the required amount of H_2O or equivalent H_2 in oceans, defined as 270 kg cm^{-2}.

Time point	Venus	Earth	Mars
Start	50	50	50
Outgassing		97	297
Veneer	205	205	
Finish	≥306	209	327
H_2O (oceans)	88	34	47

The hydrogen required to drive the blowoff, if expressed as water, is as much as 88 oceans (multiples of the present Earth ocean; Table 2). It is likely that at least some of the hydrogen was present as H_2 or H atoms in the primitive atmospheres, or as a component of hydrocarbons that were oxidized. Although the masses are large, they are still less than 3% of the total planetary masses, modest by the standards of satellites in the outer solar system (and Pluto), which contain around 50% ices.

Scenarios based on fractionation in hydrodynamic escape, of which Table 2 represents one example, have the striking ability to account for all the observed atmospheric systematics in the inner solar system. They are certainly not unique, and will certainly be refined as new knowledge accumulates. Pepin (*10*) pointed out some crucial tests, notably improved measurements of noble gases on Venus, with emphasis on isotope ratios.

A slightly less successful approach to the same questions has been made by Donahue (*15*), who noted that thermal escape could process planetary quantities of gas if it occurred on growing planetesimals instead of nearly complete planets. This scheme accounts for the elemental ratios of Ne, Ar, and Kr and the isotopic ratios of Ne, but not for the Kr/Xe ratio nor the isotopic ratios of these elements.

Mass fractionation in blowoff has almost no effect on the D/H ratio, unless the flux is in the neighborhood of the threshold for carrying mass 2 (or 3 if the major form is HD). The large observed effects, if not primordial, probably originated during later evolution.

Later Evolution

Venus. Many of the differences between Earth and Venus can be traced to the near-total lack of water on the latter. Although Venus may never have had much water in the first place, the success of the blowoff scenario discussed above points to a large initial endowment. Blowoff stops when H is no longer the dominant atmospheric constituent, either because it is nearly exhausted or, as on Earth, because it is condensed into oceans. Such condensation would not occur on Venus with the contemporary solar input, but might have occurred for one billion years or so, if the total output of the sun was really lower early in its evolution. Even after blowoff stops, the escape flux of H by other processes remains large, and the water abundance is eventually reduced to its present value or even lower. The results of such a calculation (*27*) are summarized in Fig. 2. H atoms and molecules of H_2 and H_2O are regarded as interchangeable. It is assumed that there is no barrier (such as cloud formation and precipitation) that would keep the H out of the upper atmosphere. For H mixing ratios above a percent or so, we see the last phases of blowoff or hydrodynamic escape (*28*). From that time on, the dominant loss process is probably charge exchange with hot protons; Jeans escape from Venus was negligible unless the exospheric temperature was much higher than it is now. Under present conditions (arrow at 2×10^{-6} mixing ratio) H atoms are concentrated in a nightside bulge, and this is where most of the exchange reactions occur. If there is much more H, the action shifts to the day side, and the loss rate is limited by the total rate of production of H ions. Needless to say, estimation of past rates of poorly understood processes is fraught with uncertainties. Nevertheless, the envelope of escape rates runs moderately close to the diffusion limit (dashed line), which controls the present loss rates from Earth and Mars.

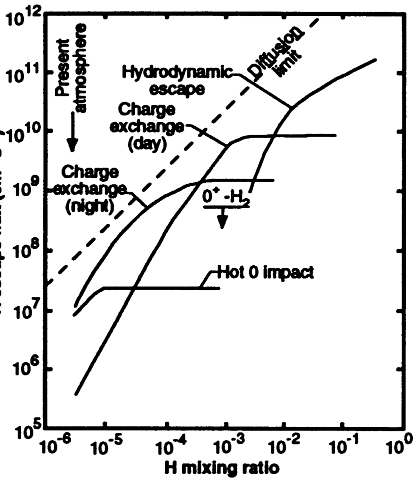

Fig. 2. Evolution of the H escape flux from Venus. The independent variable is the mixing ratio by number (mole fraction) of H, expressed in terms of H atoms. Time runs implicitly from right to left; the present is shown by the arrow at ~2 ppm. The hydrodynamic or blowoff phase is succeeded by charge exchange, first on the day side and more recently the night side, and finally supplemented by ejection by impact of fast O atoms. [Modified from (*25*)]

The processes summarized in Fig. 2 are easily able to remove all the H in an equivalent ocean, and can lead to less water and an even greater enrichment of deuterium than are observed. The likely explanation is a modest, continual supply of juvenile water, either degassed from the interior or from occasional comet impacts (*12*). An ocean-equivalent amount of H_2O could have been present, but existing data are also consistent with a considerably smaller endowment.

The blowoff phase can remove at least part of the O from dissociated H_2O. The rest must have reacted with iron in the crust, and also with any hydrocarbons and CO that might have been present. The necessary rate of turnover of fresh surface once seemed to be a serious barrier but is much more plausible in light of the radar results from Veneras 15 and 16 and Magellan, which show widespread geologically recent volcanism (*29*).

Mars. On both Earth and Mars, H is strongly inhibited by freezing and precipitation from reaching the exobase and escaping. The effect is usually called "cold trapping" by analogy with high-vacuum practice. The total loss over geologic time at the current rate happens to be nearly the same for both planets and is equivalent to the H in ~2 m of liquid. Oxygen is lost from Mars at just half the rate for H; in other words, water is escaping in pieces. This equality is maintained by a feedback process in the atmospheric chemistry near the surface, which modulates the amount of H_2 that carries H to the escape level (*30*). The principal loss process for O is dissociative recombination of O_2^+, but the exchangeable reservoir must be large, because the isotopic signature is small and not easy to comprehend (*31*).

On the other hand, both N and H show strong enrichments of the heavier isotope, a factor of 1.62 in the $^{15}N/^{14}N$ ratio and a factor of 6 in the D/H ratio, if Earth is the standard (*9*, *31*), or 60 relative to cosmic abundances. Selective loss of ^{14}N occurs by suprathermal processes, including dissociative recombination of N_2^+. Early studies (*32*) derived an initial abundance of N_2 between 1.3 and 30 mbar, and concluded that it must have been degassed early in planetary history. More recent work (*33*) finds too large an enrichment, unless the degassing was relatively recent. In any case, all but the present 0.08 mbar has been lost.

There are strong reasons to believe that Mars once had much more atmospheric CO_2 and H_2O than it now has, although perhaps not as much as shown in Table 1. (Impacts, which may have eroded even larger amounts, operated at an earlier period.) The missing quantities are probably absorbed or exist as carbonates and hydrates in the soil. The visible polar caps are thought to contain relatively small quantities. One view of carbonate formation (*34*) suggests that liquid water is necessary, at least for brief periods, to make the reaction go at a significant rate. Thus, carbonate-forming reactions would stop as soon as the atmospheric pressure fell below the triple-point pressure of water, below which liquid cannot be stable. Curiously, and perhaps significantly, this is close to the current mean pressure. More recently it has been proposed (*35*) that Mars may have had several episodes of high atmospheric pressure, warm conditions, and substantial precipitation of rain and snow, with a north polar ocean and southern glaciers. The latest episode is suggested to be Amazonian in age, an era estimated to have been somewhere between 2 and 0.5 Ga. Although the cited geological evidence is fairly strong, there remains the serious question of what could cause such a massive degassing. The suggested trigger (*35*) is widespread volcanism, some of it subsurface and accompanied by strong hydrothermal circulation, somewhat resembling processes in midocean ridges on the Earth. The CO_2 pressure would rise to a few bars, and the amount of water released would be equivalent to a global layer a few hundred meters deep, about one tenth of Earth's current ocean. After an uncertain time estimated at a few million years, water would seep back into the porous soils and lavas, the CO_2 would also be removed, and conditions resembling the present would be restored until the next episode.

Mercury and moon. The stability of heavier gases on Mercury and the moon against thermal escape depends on the exospheric temperature, which even now is almost impossible to calculate a priori. At the surface temperature, N_2 is stable on Mercury and marginally so on the moon. However, nothing could be detected until the ultraviolet spectrometer on the Mercury flyby Mariner 10 observed airglow emissions from H and He, with a marginal indication of O (*36*). Mass spectrometers landed on the moon as part of the Apollo program detected Ar and possible Ne, but H and He were not detected by a sensitive orbiting airglow experiment (*37*). Only a few years ago came the discovery of intense Na and K airglows on Mercury (*38*), followed still more recently by similar discoveries on the moon, where the intensities are much smaller (*39*). There is no doubt that all these constituents are transient; H and He escape thermally, and all atoms are rapidly photoionized on time scales of hours to a few weeks. Ions have a totally different spectral signature from their parents, and in general are not detectable optically. Moreover, they leave the atmosphere quickly because they are accelerated by a strong motional electric field that exists in the solar wind when viewed in a slow-moving reference frame.

The most reasonable sources for all the observed atoms are degassing and meteoroid impact. Implantation of H and He from the solar wind are also important, but subsequently released H may be in the undetectable molecular form. Atoms already on the surface can be released by ion sputtering and photo-sputtering, but these processes deplete the surface layers so fast that they must be replenished by one of the others, or by recycling of ions. There is still a spirited debate on the relative importance of the various processes on the two bodies.

REFERENCES AND NOTES

1. J. F. Kasting, *Science* **259**, 920 (1993).
2. G. W. Wetherill, *Annu. Rev. Earth Planet. Sci.* **18**, 205 (1990).
3. J. S. Lewis and R. G. Prinn, *Planets and their Atmospheres* (Academic Press, Orlando, FL, 1984).
4. D. M. Hunten, L. Colin, T. M. Donahue, V. I. Moroz, Eds., *Venus* (Univ. of Arizona Press, Tucson, 1983); see especially U. von Zahn, S. Kumar, H. Niemann, R. Prinn in *ibid.*, chap. 11; T. M. Donahue and J. B. Pollack in *ibid.*, chap. 29; T. M. Donahue, *Icarus* **66**, 195 (1986). Recent work on the D/H ratio is reported by C. de Bergh, B. Bézard, T. Owen, D. Crisp, J. P. Maillard, B. L. Lutz, *Science* **251**, 1547 (1991); G. Bjoraker *et al.*, *Bull. Am. Astron. Soc.* 24, 995 (1992); T. M. Donahue and R. R. Hodges, Jr., *ibid.*, p. 1003.
5. J. C. G. Walker, *Evolution of the Atmosphere* (Macmillan, New York, 1977); H. D. Holland, *The Chemistry of the Atmosphere and Oceans* (Wiley, New York, 1978).
6. H. H. Kieffer, B. M. Jakosky, C. W. Snyder, M. S.

Matthews, Eds., *Mars* (Univ. of Arizona Press, 1992); see especially R. O. Pepin and M. H. Carr, in *ibid.*, chap. 4; T. Owen, in *ibid.*, chap. 25.
7. J. F. Kasting, *Icarus* **94**, 1 (1991).
8. M. H. Carr, *ibid.* **68**, 187 (1986).
9. Y. L. Yung *et al.*, *ibid.* **76**, 146 (1989).
10. R. O. Pepin, *ibid.* **92**, 2 (1991).
11. J. Geiss and H. Reeves, *Astron. Astrophys.* **93**, 189 (1981); J. L. Linsky *et al.*, *Astrophys. J.* **402**, 694 (1993).
12. D. H. Grinspoon and J. S. Lewis, *Icarus* **74**, 21 (1988). The plausibility of a steady state depends on the fractionation factor, which is the relative efficiency of escape for H and D and must be the reciprocal of the enrichment factor. A recent evaluation by M. Gurwell and Y. L. Yung [*Bull Am. Astron. Soc.* **23**, 1194 (1991)] finds a much lower value than previously suggested and does not support a steady state with cometary water having the composition of Halley.
13. D. M. Hunten, T. M. Donahue, J. C. G. Walker, J. F. Kasting, in *Origin and Evolution of Planetary and Satellite Atmospheres*, S. K. Atreya, J. B. Pollack, M. S. Matthews, Eds. (Univ. of Arizona Press, Tucson, 1989); D. M. Hunten and T. M. Donahue, *Annu. Rev. Earth Planet. Sci.* **4**, 265 (1976).
14. J. W. Chamberlain and D. M. Hunten, *Theory of Planetary Atmospheres* (Academic Press, Orlando, 1987).
15. T. M. Donahue, *Icarus* **66**, 195 (1986).
16. D. M. Hunten, *Geophys. Res. Lett.* **12**, 271 (1985); K. J. Zahnle and J. F. Kasting, *Icarus* **68**, 462 (1986); D. M. Hunten, R. O. Pepin, J. C. G. Walker, *ibid.* **69**, 532 (1987).
17. C. Sagan and G. Mullen, *Science* **177**, 52 (1972).
18. A. I. Boothroyd, I.-J. Sackmann, W. A. Fowler, *Astrophys. J.* **377**, 318 (1991); T. E. Graedel, I.-J. Sackmann, A. I. Boothroyd, *Geophys. Res. Lett.* **18**, 1881 (1991).
19. H. J. Melosh and A. M. Vickery, *Nature* **338**, 487 (1989).
20. W. Benz, W. L. Slattery, A. G. W. Cameron, *Icarus* **74**, 516 (1988); A. G. W. Cameron, B. Fegley, Jr., W. Benz, W. L. Slattery, in *Mercury*, F. Vilas, C. R. Chapman, M. S. Matthews, Eds. (Univ. of Arizona Press, Tucson), pp. 692–708.
21. T. Owen, A. Bar-Nun, I. Kleinfeld, *Nature* **358**, 43 (1992).
22. A. P. Ingersoll, *J. Atmos. Sci.* **26**, 1191 (1969); J. F. Kasting, *Icarus* **74**, 472 (1988).
23. D. M. Hunten, *Planet. Space Sci.* **30**, 773 (1982).
24. J. G. Luhmann and J. U. Kozyra, *J. Geophys. Res.* **96**, 5457 (1991); J. G. Luhmann and S. J. Bauer, in *Venus and Mars: Atmospheres, Ionospheres, and Solar Wind Interactions*, J. G. Luhmann, M. Tatrallyay, R. O. Pepin, Eds. (American Geophysical Union, Washington, DC, 1992), p. 417; J. G. Luhmann, R. E. Johnson, M. H. G. Zhang, *Geophys. Res. Lett.* **19**, 2155 (1992).
25. D. M. Hunten, *J. Atmos. Sci.* **30**, 1481 (1973).
26. T. Matsui and Y. Abe, *Earth Moon Planets* **34**, 207 (1986); M. A. Lange and T. J. Ahrens, *Icarus* **51**, 96 (1982); T. J. Ahrens, J. D. O'Keefe, M. A. Lange, in *Origin and Evolution of Planetary and Satellite Atmospheres*, S. K. Atreya, J. B. Pollack, M. S. Matthews Eds. (Univ. of Arizona Press, Tucson, 1989), pp. 328–385.
27. S. Kumar, D. M. Hunten, J. B. Pollack, *Icarus* **55**, 369 (1983). A correction by V. A. Krasnopolsky, [*ibid.* **62**, 221 (1985)] changes some details but not the general results.
28. J. F. Kasting and J. B. Pollack, *Icarus* **53**, 470 (1983).
29. See special Magellan issues, R. S. Saunders, Ed., *J. Geophys. Res.* **97** (1992), *ibid.*, pp. 13,059 and 15,921.
30. M. B. McElroy, *Science* **175**, 443 (1972); ____ and T. M. Donahue, *ibid.* **177**, 986 (1972); S. C. Liu and T. M. Donahue, *Icarus* **28**, 231 (1976).
31. T. Owen, J. P. Maillard, C. de Bergh, B. L. Lutz, *Science* **240**, 1767 (1988). G. L. Bjoraker, M. J. Mumma, and H. P. Larson [*Bull. Am. Astron. Soc.* **21**, 991 (1989)] report a small isotope effect in the oxygen of atmospheric water vapor in which the heavier isotopes are depleted rather than enriched. H. R. Karlsson, R. N. Clayton, E. K. Gibson, Jr., and T. K. Mayeda [*Science* **255**, 1409 (1992)] show that there are reservoirs of water in SNC meteorites that are not in isotopic equilibrium with each other.
32. A. O. Nier, M. B. McElroy, Y. L. Yung, *Science* **194**, 68 (1976); M. B. McElroy, T. Y. Kong, Y. L. Yung, *J. Geophys. Res.* **82**, 4379 (1977).
33. J. L. Fox and A. Dalgarno, *Planet. Space Sci.* **28**, 41 (1980); *J. Geophys. Res.* **88**, 9027 (1983); J. L. Fox, in *Dissociative Recombination: Theory, Experiment and Applications*, J. B. A. Mitchell and F. L. Guberman, Eds. (World Scientific, Singapore, 1989), pp. 264–285; M. K. Wallis, *Earth Planet. Sci. Lett.* **93**, 321 (1989).
34. R. Kahn, *Icarus* **62**, 175 (1985).
35. V. R. Baker *et al.*, *Nature* **352**, 589 (1991).
36. A. L. Broadfoot, S. Kumar, M. J. S. Belton, M. B. McElroy, *Science* **185**, 166 (1974); A. L. Broadfoot, D. E. Shemansky, S. Kumar, *Geophys. Res. Lett.* **3**, 577 (1976).
37. R. R. Hodges, Jr., J. H. Hoffman, F. S. Johnson, *Icarus* 21, 415 (1974); R. R. Hodges, Jr., *Moon* 14, 139 (1975); W. G. Fastie, P. D. Feldman, R. C. Henry, H. W. Moos, T. M. Donahue, *Science* 182, 710 (1973).
38 A. E. Potter and T. H. Morgan, *Science* 229, 651 (1985), *Icarus* **67**, 336 (1986); D. M. Hunten, T. H. Morgan, D. E. Shemansky, in *Mercury*, F. Vilas, C. R. Chapman, M. S. Matthews, Eds. (Univ. of Arizona Press, Tucson, 1988), pp. 562–612.
39. A. E. Potter and T. H. Morgan, *Science* **241**, 675 (1988); A. L. Tyler, R. W. H. Kozlowski, D. M. Hunten, *Geophys. Res. Lett.* **15**, 1141 (1988); A. L. Sprague, R. W. H. Kozlowski, D. M. Hunten, W. K. Wells, F. A. Grosse, *Icarus* **96**, 27 (1992).
40. I acknowledge valuable comments by T. M. Donahue, B. M. Jakosky, J. F. Kasting, T. C. Owen, A. L. Sprague, Y. L. Yung, and K. J Zahnle.

Earth's Early Atmosphere

James F. Kasting

Ideas about atmospheric composition and climate on the early Earth have evolved considerably over the last 30 years, but many uncertainties still remain. It is generally agreed that the atmosphere contained little or no free oxygen initially and that oxygen concentrations increased markedly near 2.0 billion years ago, but the precise timing of and reasons for its rise remain unexplained. Likewise, it is usually conceded that the atmospheric greenhouse effect must have been higher in the past to offset reduced solar luminosity, but the levels of atmospheric carbon dioxide and other greenhouse gases required remain speculative. A better understanding of past atmospheric evolution is important to understanding the evolution of life and to predicting whether Earth-like planets might exist elsewhere in the galaxy.

A review paper on the subject of Earth's early atmosphere must, of necessity, be incomplete. A book, or perhaps several books, would be required to do justice to the topic. Here, I focus on four particular subtopics: formation of the atmosphere and ocean, the prebiotic atmosphere, long-term climate evolution, and the rise of O_2 levels. Each of these subtopics has seen an influx of new ideas over the past several years, although it would be presumptuous to claim that any of them are well understood as a result. To further limit the scope of this review, I restrict my discussion to the Precambrian Era, that is, the period before ~540 million years ago. Fluctuations in atmospheric CO_2 and O_2 levels have almost certainly occurred since that time (*1*), but these are second-order perturbations by comparison to the changes that took place earlier.

Formation of the Atmosphere and Ocean

Theories for how the atmosphere and ocean formed must begin with an idea of how the Earth itself originated. We are now reasonably certain that the terrestrial planets formed by accretion of solid materials that condensed from the solar nebula (*2*). Any primary, captured atmosphere (if one existed at all) must have been lost, as evidenced by the pronounced depletion of rare gases in Earth's atmosphere compared to cosmic abundances (*3*). The present, secondary atmosphere was generated from volatile compounds contained within the solid planetesimals from which the Earth formed. Thirty years ago, it was believed that the Earth formed relatively slowly, with a cold interior, and that most of its volatiles were originally trapped inside the planet (*4, 5*). As time passed, the Earth's interior was heated by radioactive decay, and the trapped gases were gradually released by volcanic outgassing. These volcanic gases would have been highly reduced [containing H_2, methane (CH_4), and ammonia (NH_3)] until the Earth's core formed, after which time they would have been similar to modern volcanic gases (containing H_2O, CO_2, and N_2, with traces of H_2 and CO) (*5*).

More recent models of planetary accretion (*6–8*) suggest that the Earth formed in 10 to 100 million years and that its interior was initially hot as a consequence of large impact events, including one that may have formed the moon [see papers in (*9*)]. The

The author is in the Department of Geosciences, The Pennsylvania State University, University Park, PA 16802.