THE ATMOSPHERES OF VENUS, EARTH, AND MARS: A CRITICAL COMPARISON

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INTRODUCTION

Venus, Earth, and Mars are sibling planets. They all have atmospheres, weathered surfaces, massive volcanoes, and chemically and thermally evolved interiors. Their atmospheres all possess clouds and circulate in response to the thermal forcing by the Sun, modulated by the effects of surface friction and planetary spin. Yet despite these familial characteristics, these three planets show remarkable diversity evident most dramatically in their volatile outer envelopes. We know that the Earth's nitrogen- and oxygen-rich atmosphere is a direct product of its complex biology and that its oceans and freshwater play crucial roles in this biology and in the Earth's climate. Paradoxically, the Earth's proximal neighbor Venus has a comparatively miniscule endowment of water, a carbon dioxide–rich atmosphere about 100 times more massive and with surface temperatures some 450 K warmer than the Earth's atmosphere, and no signs of life. Its next-proximal neighbor Mars shows equally few signs of atmospheric kinship; its predominantly CO_2 atmosphere has a surface pressure about 100 times less than that of Earth, its surface temperature is 60 K cooler than Earth, and it is episodically buffeted by great global storms that shroud the planet in dust.

What can we learn from these similarities and differences? First, they provide invaluable clues concerning atmospheric evolution. Our knowledge of Earth's past atmosphere is gleaned from relics in sedimentary

rocks and glacial ice, and the relics usually become more and more difficult to interpret as we go further back in time. In many cases the relic evidence is insufficient to constrain usefully our models of atmospheric evolution. Our planetary neighbors can provide further constraints, since theories developed to explain the evolution of the Earth's atmosphere also ought to yield conclusions about Venus and Mars that are in accord with observations of these planets. For example, proposals concerning the roles of cometary and asteroidal bombardment and atmospheric escape in the evolution of Earth's atmosphere should recognize that these phenomena also occur on Venus and Mars.

The atmospheric compositional extremes on these three terrestrial planets are also very informative. There is evidence that the Earth's atmosphere is subject to change on regional and global scales: first, the observed increase in atmospheric CO_2 is expected to cause a global warming; second, the observed increase in the chlorine species $CFCl_3$ and CF_2Cl_2 in the atmosphere may cause a depletion of the ozone layer; and third, the photooxidation of combustion-derived sulfur gases is causing acid rain in sensitive environments. The processes involved in these present or impending changes are not unique to Earth. The greenhouse effect due to CO_2 is important also on both Venus and Mars; on Venus the amount of CO_2 is so great that its CO_2 greenhouse is the major reason for its very highly elevated surface temperatures. Levels of HCl on Venus are about 1000 times greater than the total mixing ratio of chlorine (as $CFCl_3$, CF_2Cl_2, etc) in the Earth's ozone layer; in addition, levels of sulfur gases on Venus are some five orders of magnitude greater than those on Earth, and photooxidation of these sulfur species produces massive concentrated sulfuric acid clouds that totally shroud the planet.

The atmospheres of Venus, Earth, and Mars provide three natural experiments in geophysical fluid dynamics. Both Earth and Mars rotate rapidly on their axes, possess massive topography and surface thermal contrasts that can force atmospheric motions, and have spin equators tilted relative to the ecliptic, which produces pronounced seasons. On the other hand, Venus rotates extremely slowly on its axis, has a massive thermal inertia, has no tilt-related seasons, and receives most of its solar heating within the atmosphere rather than at the surface. Fluid-dynamical theories and numerical climate models developed for the Earth can be tested critically by application to these other atmospheres.

In this paper we discuss comparatively the physics, dynamics, chemistry, and evolution of the atmospheres of these three terrestrial planets, emphasizing the importance of comparative planetary studies for elucidating and constraining better the fundamental processes at work in planetary atmospheres.

ATMOSPHERIC STRUCTURE AND CIRCULATION

A comparison of basic meteorological parameters on Venus, Earth, and Mars is given in Table 1. Venus possesses the highest albedo of any planet in the solar system, and as a result it absorbs much less solar energy than the Earth (150 vs 240 W m^{-2}), despite its greater proximity to the Sun. Clouds are present on all three planets and play an important role in determining the albedos of the planets. (For Mars, the major clouds are composed of silicate particles, and their thickness is highly variable.) Forcing of motions by release of latent heat during cloud condensation is important only on Earth. The spin angular momentum vectors of Earth and Mars are both inclined significantly to their orbital angular momentum vectors, leading to the variations in hemispheric solar inputs over their orbital periods that produce the distinct seasons seen on both planets. At the present time the southern hemispheres of both Earth and Mars have

Table 1 Comparative meteorological parameters for the tropospheres on Venus, Earth, and Mars

	Venus	Earth	Mars
Solar constant (kW m^{-2})	2.62	1.38	0.59
Fraction of incident solar energy absorbed	0.23	0.70	0.86
Percent cloud cover	100	50	variable (dust storms)
Cloud composition	H_2SO_4	H_2O	dust, H_2O, CO_2
Orbital eccentricity	0.007	0.017	0.093
Spin inclination (obliquity)	2°36′	23°27′	25°12′
Orbital period (days)	225	365	687
Spin period (days)	243 (retrograde)	1 (prograde)	1.03 (prograde)
Solar day (days)	117	1	1.03
Gravitational acceleration (cm s^{-2})	887	980	372
Radius (km)	6051	6378	3394
Surface pressure (bars)	95	1	0.007–0.01
Surface temperature (K)	737	288	220
$d\theta/dz$ (K km^{-1})	-1 to $+5$	$+0.5$ (wet), $+3.5$ (dry)	$+2$
ΔT (equator$-$pole) (K)	5 to 15	45	90
Δh (topography) (km)	13	9	25
45° Coriolis parameter (day^{-1})	0.037	8.9	8.6
45° Rossby number (Ro)	23	0.1	0.1

summers near perihelion and thus receive more total energy over an orbital period than their northern counterparts. However, as a result of a slow precession of the longitude of the perihelia of their orbits, this situation reverses on time scales of 10,500 yr (Earth) and 25,500 yr (Mars). On both of these planets the temporal variations in the eccentricity of their orbits and in the inclination of their spin and orbital vectors (obliquity) on time scales of 10^5–10^6 yr produce oscillations in global solar energy inputs that are believed to have caused the ice ages on Earth and the successive layers of polar sedimentary deposits on Mars (Hays et al 1976, Ward 1974). These seasonal and longer-term variations in solar input are, in contrast, muted or negligible on Venus.

Venus spins very slowly on its axis compared with the rotation rates of Earth and Mars, and this has two very important effects on its atmospheric circulation. The Venus solar day (whose inverse equals the sum of the inverses of its orbital and spin periods) is 117 days compared with 1 day on Earth and Mars, and the Venus Coriolis "force" is two orders of magnitude smaller than on Earth and Mars at the same latitude. Venus also has a far greater surface temperature than Earth or Mars due to the greenhouse effect of its massive CO_2 atmosphere. As a rough approximation the surface temperature of a planet with an atmosphere in radiative equilibrium with the Sun is given by

$$T_s = \left[\frac{\alpha S}{4\sigma} \left(1 + \frac{3}{4} \tau_s \right) \right]^{1/4}, \tag{1}$$

where S is the solar constant, α is the fraction of incident solar energy absorbed by the planet, σ is Stefan's constant, and τ_s is the average (gray) infrared optical depth of the atmosphere. Evidently, to explain the T_s values in Table 1 using (1) we require a τ_s value of about 150 for Venus compared with τ_s values of only 0.8 and 0.08 for Earth and Mars. (The actual τ_s values are larger than these because the surfaces are not in radiative equilibrium.)

The convective stabilities of the lower atmospheres (tropospheres) of these three planets are quite different. Convective stability is conveniently discussed in terms of potential temperature θ, defined as the temperature that an air parcel would have if it were moved downward adiabatically to the surface. If $d\theta/dz < 0$, then the atmosphere is convectively unstable and an air parcel displaced a small vertical distance δz will have an upward acceleration $d^2z/dt^2 = -g\,\delta z\,d\ln\theta/dz > 0$. Conversely, if $d\theta/dz > 0$ then the atmosphere is convectively stable and a vertically displaced air parcel is accelerated back to its original position, subsequently oscillating about that position with a frequency equal to $(g\,d\ln\theta/dz)^{1/2}$ (the Brunt-Väisälä

frequency). On Venus $d\theta/dz$ is often very close to zero and occasionally even negative in the cloudy region between 50 and 60 km altitude (Schubert 1983). In contrast, the Earth's troposphere is generally stable, even when the additional destabilizing influence of latent heat release in a wet atmosphere is taken into account (see Table 1). Convection on Earth and Mars is a transient and patchy phenomenon, whereas it is apparently a ubiquitous phenomenon in the clouds and near the surface of Venus.

Another measure of atmospheric stability and the efficiency of motions in transporting heat is the equator to pole temperature difference ΔT. From Table 1 it is evident that the Venusian atmosphere is apparently the most efficient (and the Martian atmosphere the least efficient) at redistributing the solar energy deposited at low latitudes over the planet. This trend in efficiency is undoubtedly due in part to the very long time needed to radiatively cool the massive lower Venusian atmosphere in contrast to the time needed to move an air parcel from equator to pole (Stone 1975).

Mountains with heights Δh of several kilometers (Table 1) are present on all three of these planets, and horizontal motions must be accompanied by vertical motions forced by flow over these mountains. If the Brunt-Väisälä frequency is sufficiently large (e.g. compared with the radiative damping rate), then these forced vertical motions can produce atmospheric waves. Such topographically forced waves are evident particularly on Earth and Mars.

If a planet is rotating, an air parcel moving with horizontal velocity V will have its motion affected significantly by the rotation if its acceleration dV/dt is less than the Coriolis acceleration $4\pi V \sin \lambda/\tau$, where t is time, λ is latitude, and τ is the spin period. This comparison of scales is usually expressed in terms of the Rossby number Ro:

$$\text{Ro} = \frac{d \ln V/dt}{4\pi \sin \lambda/\tau}$$

$$= \frac{d \ln V/dt}{f}, \tag{2}$$

where $f = 4\pi \sin \lambda/\tau$ is the Coriolis parameter. Thus Ro is simply the ratio of $1/4\pi$ times the Foucault Pendulum Day to the e-folding time for velocity. If Ro < 1, then the Coriolis force is very important; evidently this is so on Earth and Mars but not on Venus (Table 1).

The latitude-height variations in tropospheric and stratospheric temperature and zonal winds for Earth (Northern Hemisphere winter–Southern Hemisphere summer) and Mars (Northern Hemisphere winter) are shown in Figures 1 and 2. There are important similarities in the temperature structures. At the surface (tropospheric) temperatures decrease
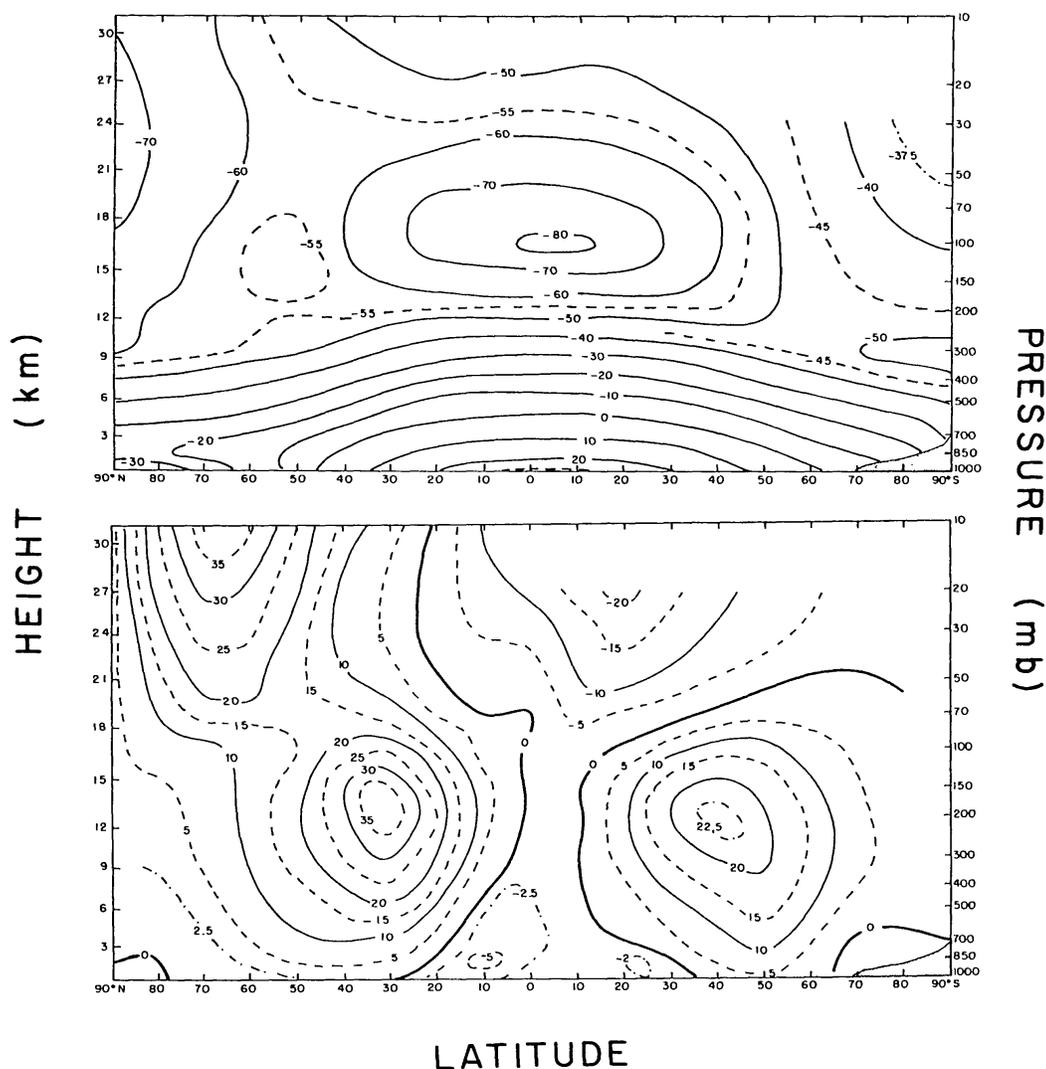
Figure 1 Observed seasonally and zonally averaged temperatures (upper graph) and zonal wind velocities (lower graph) for the atmosphere of Earth (after Newell et al 1972). Velocities are in m s^{-1} (with westerly winds positive), and temperatures are in °C. The Northern Hemisphere is in winter and the Southern Hemisphere in summer. The tropopause separating the troposphere and stratosphere lies at an altitude around 16 km at the equator and 9 km at the poles.

rapidly from equator to pole, but at lower (stratospheric) pressures (100 mbar on Earth, 0.5 mbar on Mars) the winter temperatures increase from the equator to midlatitudes. In the simplest terms, these temperature variations on both planets can be understood in the following way. Near the equatorial surface, air is heated directly or indirectly by the Sun and thus rises on the average and moves toward higher latitudes, where as a result of radiative cooling it subsides again toward the surface. The circulation is thermodynamically direct, since warm buoyant air rises and
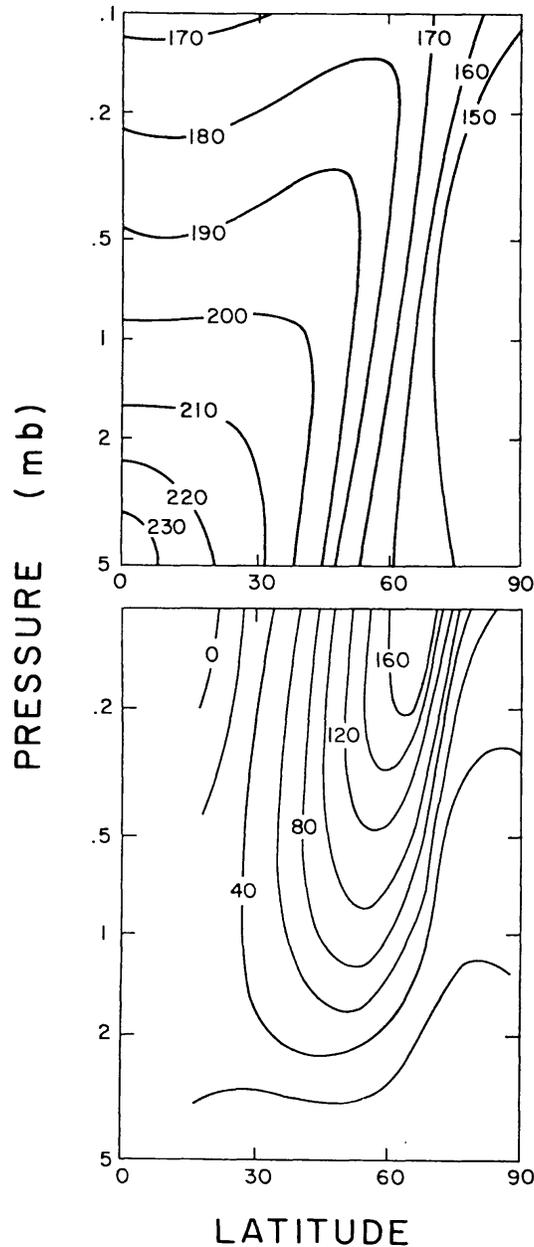
Figure 2 Observed temporally and zonally averaged temperatures (upper graph) and the zonally averaged winds deduced from them using the thermal wind equation (lower graph) as functions of latitude and altitude for a 40-day period in the late Northern Hemispheric winter on Mars (after Conrath 1981). Temperatures are in K and velocities in m s^{-1} (with westerly winds positive). The tropopause lies at about the 0.5-mbar level.

cool dense air sinks. However, in the equatorial lower stratosphere, cool air is being mechanically forced (from below) to rise and thus cool adiabatically, whereas in the midlatitude lower stratosphere warm air is being mechanically forced to sink and warm adiabatically. Thus the circulation

in the lower stratosphere is thermodynamically indirect (somewhat like a refrigerator), producing the observed paradoxical equator to midlatitude temperature increase.

Motions on Mars and Earth are both strongly affected by the Coriolis force, outside of the tropics where Ro < 1. Away from the surface, where friction is not important, steady large-scale motions are approximately geostrophic, a state in which the Coriolis force (which is perpendicular to the motion) is balanced by the horizontal pressure gradient force. Also, since vertical wind accelerations are generally small compared with the gravitational acceleration, the upward pressure gradient force is balanced approximately by the downward gravitational force (hydrostatic balance). Under these two combined states of balance, the mean zonal wind ($\bar{u}$) and temperature ($\bar{T}$) outside the tropics are related by the thermal wind equation

$$\frac{\partial \bar{u}}{\partial \ln P} = \frac{R}{f}\left(\frac{\partial \bar{T}}{\partial y}\right)_P, \tag{3}$$

where P is pressure, R is the gas constant, and y is the meridional (equator-pole) coordinate. Inspection of $\bar{T}$ and $\bar{u}$ for the Earth shown in Figure 1 demonstrates the reality of Equation (3). In particular, $\partial \bar{T}/\partial y < 0$ in the troposphere so $\bar{u}$ increases with decreasing pressure, while $\partial \bar{T}/\partial y > 0$ in the lower stratosphere so $\bar{u}$ decreases with decreasing pressure; the result is the familiar westerly jet stream in the upper troposphere. A similar change in the sign of $\partial \bar{T}/\partial y$ between the middle stratosphere and mesosphere is associated with the presence of the stratospheric westerly polar night jet and easterly summer jet (both evident in Figure 1). For Mars we expect a similar adherence to the thermal wind equation, and the $\bar{u}$ values shown in Figure 2 are in fact derived from the observed temperatures using this equation.

Wave motions in the form of traveling cyclones and anticyclones are very familiar on Earth (Palmen & Newton 1969) and are also evident on Mars (Conrath 1981). On Earth, maximum wave activity occurs during the winter months, and these waves are generated as a result of instabilities of zonal flows in states where isobaric surfaces are inclined to isothermal surfaces [the so-called baroclinic instability; see Holton (1972) for a review]. These traveling waves, which are approximately geostrophic (i.e. quasi-geostrophic) are largely responsible for the observed atmospheric transport of heat from tropical to polar regions. Quasi-geostrophic waves are also forced by topography and by ocean-land temperature contrasts, and in this case these waves are usually stationary and of planetary scale. Both strong high-altitude westerly winds and high-altitude easterly winds

on Earth and Mars serve to effectively reflect downward all but the largest scale quasi-geostrophic waves, thus trapping them in the lower atmosphere (Charney & Drazin 1961, Conrath 1981).

While there are certain similarities between the circulations of Earth and Mars, there are also a number of differences that should be emphasized. Mars has episodic global-scale dust storms forced by absorption of solar radiation by wind-raised dust (Gierasch 1974, Zurek 1982), and there are no analogous events to these on Earth. Conversely, the stability and thermodynamics of the Earth's atmosphere are affected very strongly by latent heat release evident most dramatically in hurricanes, typhoons, and intense tropical convective storms (see Holton 1972), whereas latent heating is unimportant on Mars (and on Venus). Temperatures increase upward in the stratosphere on Earth as a result of the absorption of near-ultraviolet and visible solar radiation by the ozone layer, but there is no analogous Martian (or Venusian) stratospheric near-ultraviolet absorber. The oceans on Earth (and the lower atmosphere on Venus) have a large thermal inertia that serves to modulate diurnal and seasonal surface temperature variations, while such a modulation mechanism is not present on Mars.

Temperature and zonal wind structures in the Venusian atmosphere are given in Figures 3 and 4. The large Rossby number on Venus means that the geostrophic balance and thermal wind relation are not valid on this planet. Temperature drops steadily with altitude in the troposphere and strato-mesosphere up to 100 km. Above this level, absorption of solar ultraviolet (UV) photons by CO_2 during the long Venusian day produces an increase in temperature with altitude in the thermosphere. The hot thermosphere totally disappears at night, because cooling by radiation and downward transport of heat apparently occurs on time scales short compared with the Venusian night. In contrast, on Earth and Mars the hot thermosphere, although cooled, is still maintained over the relatively short night. (On Earth, O_2 is the major thermospheric UV absorber, and on Mars it is CO_2.)

The zonal-average winds $\bar{u}$ on Venus are remarkable in that the entire atmosphere superrotates in the same (retrograde) direction as the planet. At the cloud-top altitude of 70 km the zonal velocity is 120 m s^{-1}, so cloud-top features rotate around the planet in only 4 days compared with the planet's spin period of 243 days. For comparison, the Earth (Figure 1) has both westerly winds rotating in the same (prograde) direction as the planet and easterly winds rotating in the opposite (retrograde) direction. Westerly angular momentum is canceled to a large extent by easterly angular momentum, so that total angular momentum in the Earth's atmosphere is over two orders of magnitude less than on Venus.
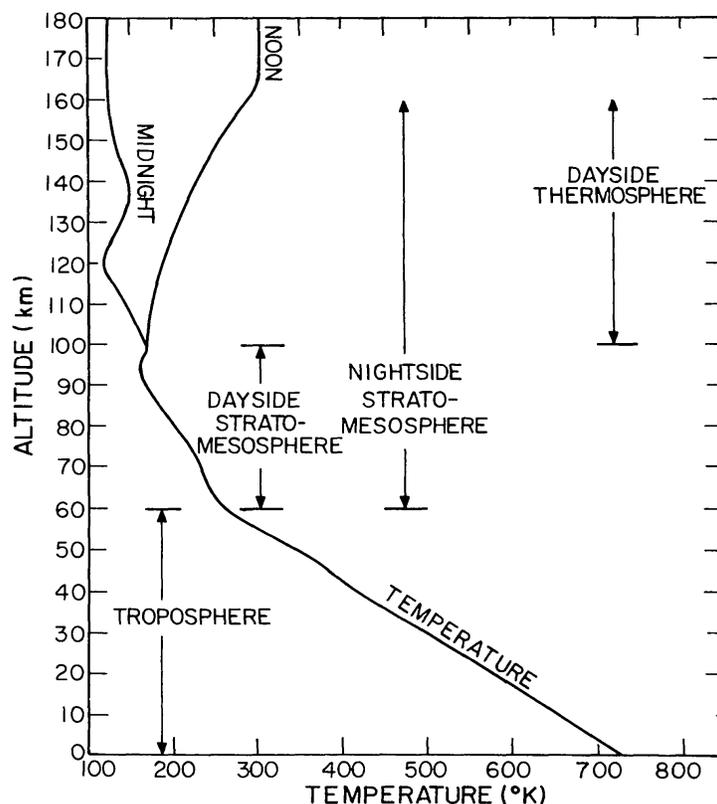
Figure 3 Variation of temperature with altitude at 30° latitude on Venus in the standard atmosphere of Seiff (1983). Also shown are various regions of the atmosphere as discussed in the text. The Venus sulfuric acid clouds lie between 50 and 70 km altitude.

Maintenance of the superrotation of the Venusian atmosphere against down-gradient vertical diffusion of momentum is not fully understood, although there are a number of hypotheses concerning ways in which forced eddy or wave motions can transport zonal momentum in the required upward direction (see Schubert 1983). Waves on Venus (i.e. motions not having zonal symmetry) are observed in UV cloud images, and their dynamic properties have been analyzed (e.g. Rossow et al 1980). As on Earth and Mars, waves on a wide variety of space and time scales are expected on Venus as a result of either thermal forcing by the Sun (producing tides, etc) or mechanical forcing caused by convection or flow over mountains.

The strong zonal winds $\bar{u}$ in the Venusian atmosphere produce a significant equatorward centrifugal force, while higher temperatures at the equator than at the pole produce a significant poleward pressure-gradient force. (This is best visualized by taking a polar view of the zonal wind flow.) Leovy (1973) suggested correctly that these two forces are approximately in
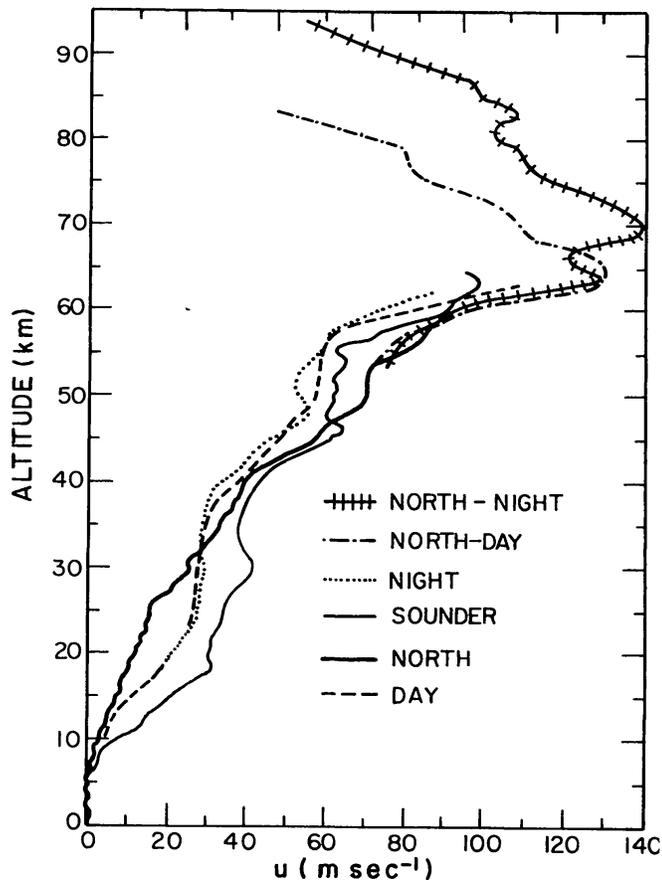
Figure 4   Retrograde zonal wind velocity u as a function of altitude on Venus. The values were obtained by tracking the four Pioneer Venus entry probes (designated night, sounder, north, and day) and by using the temperatures from the north plus night or north plus day entry probes and then deducing the wind velocity from them by using the cyclostrophic thermal wind equation (Counselman et al 1980, Seiff 1983).

balance on Venus. This so-called cyclostrophic balance is familiar on Earth in intense tropical cyclones, where Ro > 1. Combining the cyclostrophic balance with the hydrostatic balance yields an equation analogous to the thermal wind equation (3):

$$\frac{\partial \bar{u}}{\partial \ln P} = \frac{R}{2\bar{u} \tan \lambda} \left(\frac{\partial \bar{T}}{\partial \lambda}\right)_P, \tag{4}$$

where λ is latitude (Schubert 1983). A comparison of the directly measured winds in the 55–65 km region with those deduced using (4) and the observed latitudinal temperature gradients indicates good agreement (see Figure 4). In particular, as required by (4), $\bar{u}$ increases with decreasing pressure, while temperature decreases from equator to pole at these altitudes on Venus.

ATMOSPHERIC COMPOSITION AND CHEMISTRY

The abundances of the known gases in the atmospheres of Earth, Venus, and Mars are summarized in Tables 2–4, along with information about their sources and sinks where available and relevant. In view of the major objective of this review, we do not attempt a detailed discussion of the chemistry of all the listed species. Appropriate comprehensive discussions of atmospheric chemistry on these three planets are already available (Lewis & Prinn 1984, Levine 1985). Instead, we focus on certain topics where the value of a comparative study of these three atmospheres is particularly fruitful. First, we address the role of living organisms in atmospheric chemical cycles by comparing and contrasting the Earth's

Table 2 Composition of the Earth's nonurban troposphere and the major processes that currently control it (Graedel 1978, Lewis & Prinn 1984)

Gas	Volume mixing ratio	Major source	Major sink
N_2	7.81×10^{-1}[a]	Biology	Biology
O_2	2.09×10^{-1}[a]	Biology	Biology
^{40}Ar	9.3×10^{-3}[a]	Outgassing (^{40}K)	—
H_2O	$\leq 4 \times 10^{-2}$	Evaporation	Condensation
CO_2	3.4×10^{-4}	Combustion, biology	Biology
$^{36,38}Ar$	3.7×10^{-5}	Outgassing (primordial)	—
$^{20,22}Ne$	1.82×10^{-5}	Outgassing (primordial)	—
^4He	5.24×10^{-6}	Outgassing (U, Th)	Escape
CH_4	$1.7–3 \times 10^{-6}$	Biology	Photooxidation
$^{80,82-84,86}Kr$	1.14×10^{-6}	Outgassing (^{235}U)	—
H_2	5×10^{-7}	Photochemistry (H_2O)	Escape (as H)
N_2O	3.1×10^{-7}	Biology	Photodissociation
C_2H_4, etc	$\leq 7 \times 10^{-7}$	Incomplete combustion	Photooxidation
C_2H_2, etc	$\leq 2 \times 10^{-7}$	Incomplete combustion	Photooxidation
C_4H_{10}, etc	$\leq 2 \times 10^{-7}$	Incomplete combustion	Photooxidation
Toluene, etc	$\leq 1 \times 10^{-7}$	Incomplete combustion	Photooxidation
CO	$(0.4–2) \times 10^{-7}$	Photochemistry	Photochemistry
$^{128-132,134,136}Xe$	8.7×10^{-8}	Outgassing (U, I)	—
O_3	$(0.1–1) \times 10^{-7}$	Photochemistry (NO_2)	Photochemistry
CH_3O_2H, etc	$\simeq 10^{-9}$	Photochemistry	Photochemistry
HCl	$\simeq 1 \times 10^{-9}$	Acidification (sea salt)	Rainout
NH_3	$(0.1–1) \times 10^{-9}$	Biology	Photooxidation
HNO_3	$(0.05–1) \times 10^{-9}$	Photochemistry (NO_2)	Rainout
COS	5×10^{-10}	Biology	Photodissociation
CH_3Cl	5×10^{-10}	Biology	Photooxidation
NO, NO_2	$(0.2–5) \times 10^{-10}$	Combustion, biology	Photooxidation
$(CH_3)_2S$	$\simeq 4 \times 10^{-10}$	Biology	Photooxidation
CF_2Cl_2	3.7×10^{-10}	Industry	Photodissociation
SO_2	$\simeq 3 \times 10^{-10}$	Combustion, photochemistry	Photooxidation
$CFCl_3$	2.2×10^{-10}	Industry	Photodissociation
H_2S	$\simeq 2 \times 10^{-10}$	Biology	Photooxidation

[a] Values quoted are for dry air.

Table 3 Composition of the Venusian troposphere and the (probable) major processes that control it (von Zahn et al 1983, Moroz 1983, Prinn 1985)

Gas	Volume mixing ratio	Major source	Major sink
CO_2	9.65×10^{-1}	Outgassing	$CaCO_3$ formation?
N_2	3.5×10^{-2}	Outgassing	—
CO	2×10^{-5} (22 km), 10^{-3} (100 km)	Photochemistry (CO_2)	Photooxidation
SO_2	1.5×10^{-4} (22 km), 5×10^{-8} (70 km)	Photochemistry	$CaSO_4$ formation
^{36,38}Ar	3.7×10^{-5}	Outgassing (primordial)	—
^{40}Ar	3.3×10^{-5}	Outgassing (^{40}K)	—
H_2O	10^{-4} (22 km), $(1-40) \times 10^{-6}$ (70 km)	Outgassing, impacts	Silicate hydration, Fe^{++} oxidation plus H escape
H_2	$\leq 2.5 \times 10^{-5}$[a]	Photochemistry	Escape (as H)
^{4}He	1.2×10^{-5}	Outgassing (U, Th)	Slow escape
H_2S	$(3-40) \times 10^{-6}$[a]	Outgassing (FeS_2)	Photooxidation
COS	$\leq 4 \times 10^{-5}$[a]	Outgassing (FeS_2)	Photooxidation
^{20,22}Ne	7×10^{-6}	Outgassing (primordial)	—
$^{80,82-84,86}$Kr	$7 \times 10^{-7}, 5 \times 10^{-8}$[a]	Outgassing (primordial, ^{235}U)	—
HCl	4×10^{-7}	Outgassing (NaCl)	NaCl formation
HF	5×10^{-9}	Outgassing (CaF_2)	CaF_2 formation

[a] Important disagreements exist between the different instruments that have measured these species.

atmospheric composition to the atmospheric compositions on Venus and Mars, which are determined by strictly abiotic processes. We then discuss three chemical cycles: the sulfur cycles on Venus and Earth, the chlorine-catalyzed cycles on Venus and Earth, and the major photooxidation (hydroxyl radical) cycles on Earth, Mars, and Venus. Finally, we address recent evidence for contemporary global-scale compositional changes on all three planets.

Biology and Atmospheric Composition

As summarized in Tables 2–4, the major components of the Earth's atmosphere are currently controlled by biological processes, whereas the Venusian and Martian atmospheres are controlled by strictly abiotic processes. On Earth, the major N_2 source is the denitrifying bacteria in soils and oceans that convert ammonium and nitrate compounds into N_2. The rates are such that the present atmospheric N_2 amount is produced in about 17 Myr. At the same time, a combination of the activities of nitrogen-fixing bacteria such as those in legume root nodules (which convert atmospheric N_2 into NH_4^+, NO_3^-, and organic nitrogen), together with the abiological processes of lightning and combustion (which convert atmospheric N_2 and O_2 into NO and NO_2, which rain out ultimately as HNO_3), serves to

Table 4 Composition of the Martian troposphere and the (probable) major processes that control it (Barth 1985, Lewis & Prinn 1984)

Gas	Volume mixing ratio	Major source	Major sink
CO_2	9.53×10^{-1}	Evaporation, outgassing	Condensation
N_2	2.7×10^{-2}	Outgassing	Escape (as N)
^{40}Ar	1.6×10^{-2}	Outgassing (^{40}K)	—
O_2	1.3×10^{-3}	Photochemistry (CO_2)	Photoreduction
CO	7×10^{-4}	Photochemistry (CO_2)	Photooxidation
H_2O	$\simeq 3 \times 10^{-4}$	Evaporation, desorption	Condensation, adsorption
$^{20,22}Ne$	2.5×10^{-6}	Outgassing (primordial)	—
^{36}Ar	5×10^{-6}	Outgassing (primordial)	—
Kr	3×10^{-7}	Outgassing (primordial, ^{235}U)	—
Xe	8×10^{-8}	Outgassing (primordial, U, I)	—
O_3	$(0.1–20) \times 10^{-8}$	Photochemistry (CO_2)	Photochemistry
NO	7×10^{-5} (120 km)	Photochemistry (N_2, CO_2)	Photochemistry

remove the current N_2 amount on about the same time scale. If we totally remove the biological processes, then lightning and combustion continued at *current* rates would remove all the atmospheric N_2 in about 80 Myr.

Would the Earth without life therefore lose its N_2 atmosphere? To help answer this question, we could look at our two planetary neighbors and observe that the surface pressure of N_2 on Venus is 3 bars and that N_2 is 2.7% of the atmosphere. Evidently, N_2 can exist without biological activity.

The abiotic removal rates of N_2 by combustion and lightning in the current atmosphere bear little resemblance to those that would occur in the absence of biology. First, there would be no organic material to fuel combustion. Second, the yield of NO in lightning strokes depends sensitively on the total oxygen mixing ratio (the same is true for two other N_2 sinks, namely production of NO from N_2 by cosmic ray and extreme UV bombardment of the upper atmosphere). The major atmospheric oxygen-bearing species are O_2, H_2O, and CO_2. Water vapor is controlled by simple evaporation-condensation. Atmospheric O_2 and CO_2 are currently under biological control, with the opposing biological processes of photosynthesis and respiration/decay producing and removing the Earth's O_2 and CO_2 on time scales of about 3000 and 5 yr, respectively. In the absence of biology, CO_2 levels are not likely to be very much different than those currently observed as long as the oceans exist to buffer CO_2 through carbonate formation. However, only very small amounts (parts per million or less) of O_2 are expected on an abiotic Earth due to UV photodissociation of CO_2 and H_2O (Levine 1985). Such abiotic O_2 production is in fact the major source of O_2 on Mars and Venus today [see reviews by Barth (1985) and Prinn (1985)], but O_2 is only 0.13% of the Martian atmosphere and

has never been definitively observed on Venus. Evidently, on a lifeless Earth the major oxygen sources would be H_2O not O_2 in lightning strokes, and CO_2 not O_2 in upper atmospheric cosmic ray and extreme UV processes. Thus, the abiotic N_2 removal rates will be at least one or two orders of magnitude less than today, and the lifetimes of N_2 therefore longer than 1 Gyr rather than as short as 80 Myr. In addition, whatever N_2 is removed through HNO_3 rainout and sedimentary nitrate formation can be recycled through plate subduction and associated volcanism, processes that operate on time scales of 100 Myr.

Apparently, biological processes are therefore essential for maintaining high levels of O_2 in the Earth's atmosphere but not high levels of N_2, CO_2, and H_2O. For the many reactive trace species at levels of parts per million or less, it is evident from Table 2 that the major sources are almost exclusively biological or industrial, and the major sinks almost exclusively are photooxidation or photodissociation. As we discuss shortly, photooxidation of reduced species depends strongly on ambient O_3 (and thus O_2 levels). Thus (as we have emphasized for N_2) removal of all the biological sources is accompanied by a short reduction in the efficiency of the photooxidation sink, making predictions of the levels of these trace species on a lifeless Earth much more difficult. Nevertheless, for species such as the hydrocarbons for which the only known significant sources are biological in origin it is safe to predict that their levels will be much lower despite the less oxidizing nature of the lifeless environment. The same is true for biogenic and anthropogenic species like N_2O, COS, $CFCl_3$, and CF_2Cl_2, whose principal sinks are photodissociation reactions whose rates would actually increase at low O_2 (and thus low O_3) levels.

Chemical Cycles and Atmospheric Composition

SULFUR CYCLES ON EARTH AND VENUS   On Earth we are becoming increasingly aware of the environmental importance of the sulfur cycle (see Duce et al 1984). As depicted in Figure 5, sulfur is injected directly into the atmosphere as SO_2 from fossil-fuel combustion. (Volcanoes are minor in comparison.) Sulfur is also injected in the form of the chemically reduced species $(CH_3)_2S$, CS_2, H_2S, and COS as a result of microbial activity in the oceans and in marshlands (Andreae & Raemdonck 1983, Carroll et al 1986); putatively, the emissions of these reduced species are comparable to SO_2 emissions on a global scale. Successive oxidation reactions involving the OH and NO_3 radicals and UV photons ($h\nu$) serve to convert the reduced species (with the exception of COS) to SO_2 on time scales of hours to days. Further oxidation reactions in the gas phase and in droplets then convert the photochemically produced and combustion-derived SO_2 to H_2SO_4 on a time scale of a few days. The H_2SO_4 rains out as a dilute acid, and
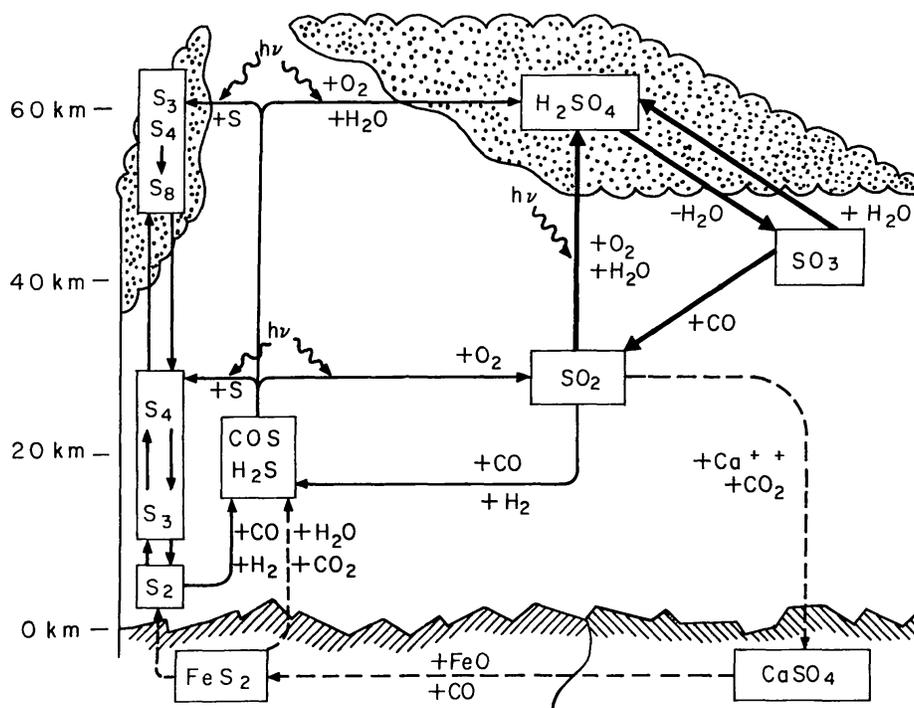
Figure 5   The cycle of sulfur compounds in the Earth's atmosphere. The ocean and marshlands are important sources of H_2S, $(CH_3)_2S$, CS_2, and COS, while fossil-fuel combustion and volcanoes produce SO_2. These source species are converted by a variety of reactions into short-lived species (enclosed in circles) and thence either to SO_2 or to various organic sulfoxyl compounds. The SO_2 is oxidized to yield concentrated sulfuric acid particles in the stratosphere and dilute sulfuric acid particles in the trophosphere. Eventually all these product species are rained out or absorbed at the surface.

because the sources of SO_2 are geographically very patchy and the SO_2 lifetime is short, this acid rain is also geographically patchy and has greatest fluxes within 1000 km or so of SO_2 source regions.

The lifetime of COS is significantly longer than those of the other sulfur species, and it can therefore be transported horizontally over global scales and vertically into the stratosphere before being destroyed. In the stratosphere, COS photodissociates to yield SO_2 and thence concentrated sulfuric acid particles (Crutzen 1976); these particles form a very thin global-scale layer in the stratosphere called the Junge layer. Episodically, volcanoes inject SO_2 rapidly and directly into the stratosphere, providing a transient additional source of sulfuric acid.

Since the presence of sulfur species in our atmosphere is associated with microbial and human activity, we would not expect to see sulfur gases on Venus and Mars. In fact, sulfur gases on Venus have mixing ratios about 10^6 times greater and total amounts about 10^8 times greater than on Earth!

As depicted in Figure 6, the source of Venusian sulfur gases putatively involves reactions between atmospheric CO_2, H_2O, and sulfur-containing minerals such as pyrite (FeS_2) contained in volcanically derived surface lavas or within volcanoes. The emitted gases are COS, H_2S, and to a lesser extent SO_2. The existence of this source depends on the combination of (*a*) a very hot and chemically reduced surface relative to the Earth and (*b*) extant volcanism. Photochemical reactions driven by UV photons (hν) convert COS and H_2S to elemental sulfur and (using oxygen derived from CO_2 photodissociation) to SO_2 (Prinn 1973). The SO_2, which is the dominant atmospheric sulfur-bearing gas, is oxidized to sulfuric acid particles (see Yung & DeMore 1982), which form a low-density haze in the 50–70 km altitude region that totally shrouds the planet. The formation of UV-absorbing elemental sulfur particles along with the sulfuric acid provides a plausible cause of the distinct absorption patterns observed in UV images of the planet. The net oxidation of COS and H_2S leads to a SO_2 concentration that exceeds its value in equilibrium with calcium-bearing surface minerals. Various weathering reactions therefore proceed,

Figure 6   The cycle of sulfur compounds in the Venusian atmosphere (Prinn 1985). Volcanic eruptions or reactions of H_2O and CO_2 with volcanic surface rocks yields COS, H_2S, S_2, and SO_2. Various photochemical reactions convert these species to concentrated H_2SO_4 or elemental sulfur particles in the Venusian clouds. The H_2SO_4 evaporates at the cloud base, producing SO_3, which can then either recondense or be reduced to SO_2. Reactions of SO_2 with Ca^{2+} in rocks provides a sink that must be balanced by the volcanic and surface sources.

involving the leaching of calcium from surface minerals to form anhydrite ($CaSO_4$). X-ray fluorescence measurements indicate that Ca^{2+} is several times more abundant than SO_4^{2-} in Venusian surface rocks, so there is ample CaO available for removing SO_2.

There are obviously many informative comparisons to be made between these two sulfur cycles. The Venusian clouds, in both composition and mode of formation, are not unlike an enormously exaggerated version of the Earth's Junge layer. The role of human and microbial processes on Earth in recycling sulfates and organic sulfur into the atmosphere can be compared to the role of geological processes on Venus in recycling sulfur in buried calcium sulfate into pyrite and thence back into gaseous sulfur compounds. Finally, while the photooxidation processes are similar, the very large amounts of sulfur gases on Venus lead to long time scales in the Venusian cycle relative to Earth; in particular, the lifetime for SO_2 oxidation to H_2SO_4 is about 200 yr on Venus compared with a few days on Earth.

CHLORINE CYCLES ON VENUS AND EARTH   Chlorine as HCl is remarkably abundant on Venus (Table 3). Unlike SO_2 on Venus, the observed HCl abundance is rather close to that expected for equilibrium at the hot surface between HCl, aluminosilicates, H_2O, and halite (Lewis 1970). Unlike the sulfur gases, extant volcanism is therefore not required to sustain the HCl. The Earth's atmosphere also contains chlorine compounds, most notably in the form of CH_3Cl (produced naturally by marine microorganisms) and the synthetic (freon) gases $CFCl_3$ and CF_2Cl_2 (Table 2). The levels of chlorine on Venus are about 1000 times greater than those on Earth, but on both planets the chlorine species play important roles as sources of catalysts for photochemical reactions [see Prinn (1971) for Venus; Stolarski & Cicerone (1974) and Molina & Rowland (1974) for Earth].

On Earth the compounds CH_3Cl, CF_2Cl_2, $CFCl_3$, and other chlorofluorocarbons and hydrochlorofluorocarbons are emitted at the surface, and since their lifetimes range from decades to a century or more, they are transported up to the stratospheric ozone layer (altitudes of 20–40 km) without being significantly depleted. There, these species are destroyed by photodissociation and reaction with $O(^1D)$ and (for the hydrogen-containing species such as CH_3Cl) by reaction with OH (see Figure 7). This leads to production of Cl atoms. The following chlorine atom-conserving catalytic reactions

$$Cl + O_3 \rightarrow ClO + O_2,$$

$$h\nu + O_3 \rightarrow O + O_2,$$

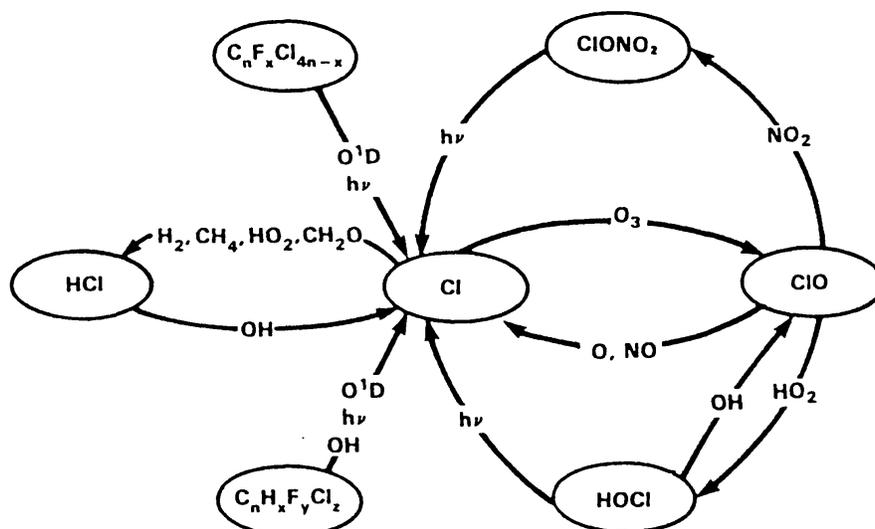$$ClO + O \rightarrow Cl + O_2,$$
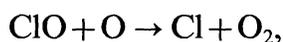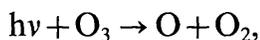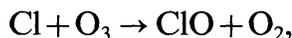
Figure 7 The roles of chlorine compounds in the Earth's stratospheric ozone layer. Chlorofluorocarbons ($C_nF_xCl_{4n-x}$) and hydrochlorofluorocarbons ($C_nH_xF_yCl_z$) produce Cl atoms and ClO radicals that catalytically destroy ozone. Formation of HCl moderates this catalytic destruction (after Watson et al 1986).

then convert two O_3 molecules into three O_2 molecules. The catalytic destruction is partially short-circuited by the reaction of ClO with NO instead of O, and the concentrations of destructive Cl and ClO are decreased by formation of temporary reservoir species HCl, $ClONO_2$, and HOCl.

On Venus, HCl like the freon gases photodissociates in the stratosphere above the clouds to produce Cl atoms. Current ideas are summarized in Figure 8. The Cl atoms form ClO by reaction with O_3, as on Earth, but since O_3 levels are much less on Venus than Earth the ratio of Cl to ClO is $\gg 1$ on Venus while $\ll 1$ on Earth. Large CO and Cl abundances on Venus lead to ClCO and $COCl_2$ formation. Yung & DeMore (1982) have proposed that the formation of $ClCO_3$ from CO, Cl, and O_2 followed by its decomposition to CO_2 and ClO is an important pathway for recombining the CO and O produced by CO_2 photodissociation on this planet.

OXIDATION CYCLES ON EARTH, MARS, AND VENUS In the Earth's troposphere the major oxidizer is the OH radical (Levy 1971, Duce et al 1984). As depicted in Figure 9, OH is produced primarily by reaction of excited oxygen atoms $O(^1D)$ with water vapor H_2O and removed primarily by reactions with CO. The $O(^1D)$ is produced by photodissociation of O_3 by UV light with wavelengths <310 nm. The ozone is produced in turn by photodissociation of NO_2 when NO_2 levels are sufficiently high (Chameides & Walker 1973) or by transport down from the stratosphere (where it was produced by O_2 photodissociation). As we have already noted, the
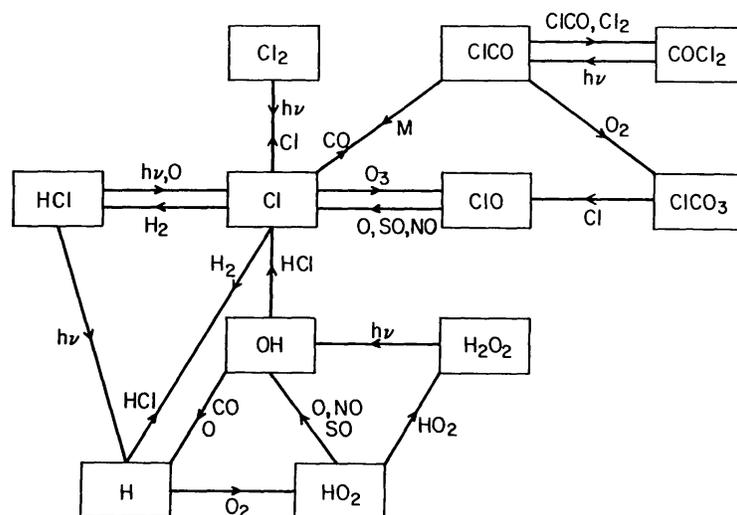
Figure 8 The roles of chlorine and hydrogen compounds in the Venus stratomesosphere. HCl photodissociation produces Cl and H, which then initiate a variety of reactions that recombine CO, O, and O_2 (after Yung & DeMore 1982).
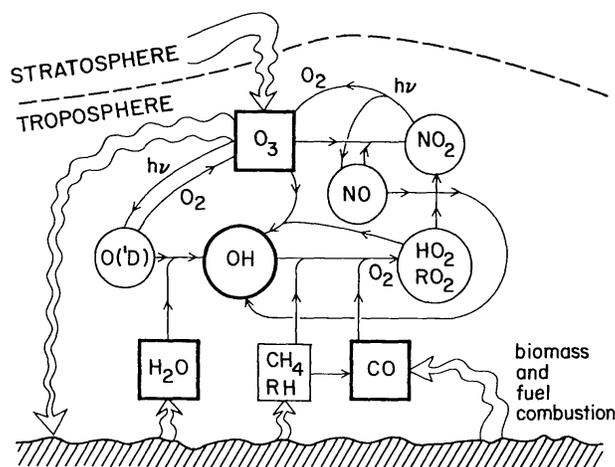

Figure 9 The major oxidation cycle in the Earth's troposphere. The cycle is initiated by the combination of sunlight, H_2O, and ozone that is produced locally from NO_2 or transported down from the ozone layer. The major oxidizer is the OH radical, which is responsible for oxidation of most atmospheric trace species emitted from the surface, including hydrocarbons, CO, and sulfur gases.

composition of the Earth's atmosphere is determined to an important degree by the rate of tropospheric oxidation of biogenic gases by OH.

A remarkably similar oxidation mechanism operates on Mars, where it is responsible for reformation of the CO_2 destroyed by photodissociation (McElroy & Donahue 1972, Parkinson & Hunten 1972). As illustrated in

Figure 10, the major oxidizer is again OH, formed initially by dissociation of H_2O. Once formed, however, it enters a catalytic cycle

$$CO + OH \rightarrow CO_2 + H,$$

$$H + O_2 + M \rightarrow HO_2 + M,$$

$$O + HO_2 \rightarrow OH + O_2,$$
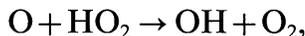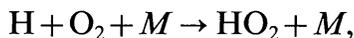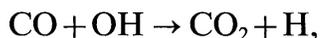
(where M is any molecule) which serves to combine CO and O to form CO_2 with conservation of the OH, H, and HO_2. The same catalytic cycle also occurs on Venus, where it is initiated by the H atoms from HCl photodissociation (see Figure 8). The reaction of O with HO_2 is not important in Earth's trophosphere, and the above catalytic cycle is replaced on Earth by the more complex and less efficient cycle depicted in Figure 9 requiring NO_2 photodissociation and O_3 formation.

Global Changes in Atmospheric Composition

Observations made principally over the last decade have challenged the traditional viewpoint that global atmospheric composition is stable on time scales less than a million years or so. On Earth, the long-lived atmospheric gases CO_2, N_2O, CH_4, $CFCl_3$, CF_2Cl_2, CH_3CCl_3, and CCl_4 are observed today to be increasing over the globe at average rates of about 0.34, 0.26, 1.0, 5.1, 5.0, 6.7, and 1.3% per year, respectively (Komhyr et al 1985, Blake & Rowland 1986, Prinn et al 1983, Cunnold et al 1986). These increases represent a current imbalance between the sources and sinks for these gases (as summarized in Table 2). Some of the imbalances are well understood (e.g. the known industrial source of $CFCl_3$ exceeds its known photodissociation sink), while others are very poorly understood (e.g. is the CH_4 increase due to an increase in microbial production of CH_4
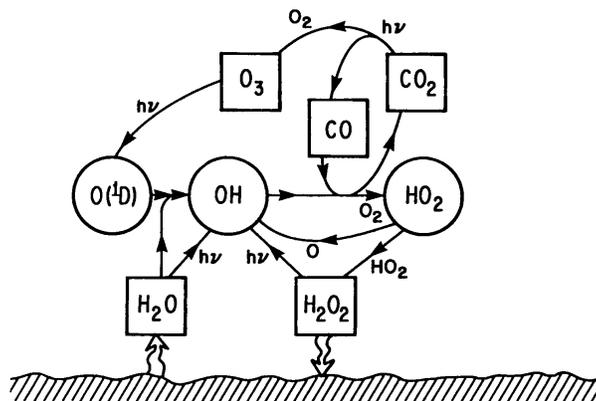

Figure 10   The major oxidation cycle in the Martian atmosphere. The cycle is initiated by photodissociation of H_2O, producing OH that oxidizes CO back to CO_2.

or to a decrease in photochemical destruction of CH_4 resulting from decreasing atmospheric OH levels?) All of the above long-lived gases are important in the Earth's greenhouse effect, and if today's rates of increase are extrapolated into the future a global surface warming of a few degrees Kelvin is predicted early in the next century (Ramanathan et al 1985). All of these gases are also important in the chemistry of the ozone layer through production or removal of catalysts and/or through radiative effects.

Global changes on these short time frames are not confined to Earth (see Figure 11). The global average abundance of SO_2 in the visible part of the Venusian atmosphere decreased tenfold between 1978 and 1983 putatively as a result of the recovery of the atmosphere from a massive (circa 1978) volcanic eruption with important implications for the Venus sulfur cycle (Esposito 1984). The dust-loading in the Martian atmosphere (as measured by the vertical optical depth of the atmosphere) increased fivefold as a result of a mid-1977 global dust storm with very important effects on global Martian climate (Pollack et al 1979).

ATMOSPHERIC ORIGIN AND EVOLUTION

A central problem presented to us by Venus, Earth, and Mars is to explain how these three very different atmospheres can be derived from the same parent material—the cloud of gas and dust making up the solar nebula. The magnitude of this problem is only fully realized when one considers that about 98% (by mass) of the solar nebula was $H_2 + He$, and that only 2% was made up of the volatiles and grains that eventually formed these three planets and their atmospheres. Indeed, no completely satisfactory solution has yet been found after years of work by many investigators. Recent reviews by Lewis & Prinn (1984) and Black & Matthews (1985) describe this work from a variety of perspectives. Instead of repeating these discussions, we review the chemical and physical processes influencing atmospheric origin and evolution, emphasizing in particular the roles of common evolutionary processes.

Figure 11 Examples of global changes on Venus, Earth, and Mars. (*a*) Global-mean concentration of SO_2 at the 40-mbar level on Venus as a function of time (measured in days) beginning at the arrival time of the Pioneer Venus Orbiter on 4 December 1978 (after Esposito 1984). (*b*) Concentration of the freon gas $CFCl_3$ at two remote locations on Earth as measured by the ALE/GAGE trace-gas network (Prinn et al 1983, Cunnold et al 1986). (*c*) Optical depth of the atmosphere at the Viking I Lander site on Mars as a function of time measured in Martian days (1.03 Earth days) beginning on the Viking landing date (20 July 1976). A great dust storm began on about Martian day 310 (after Pollack et al 1979).
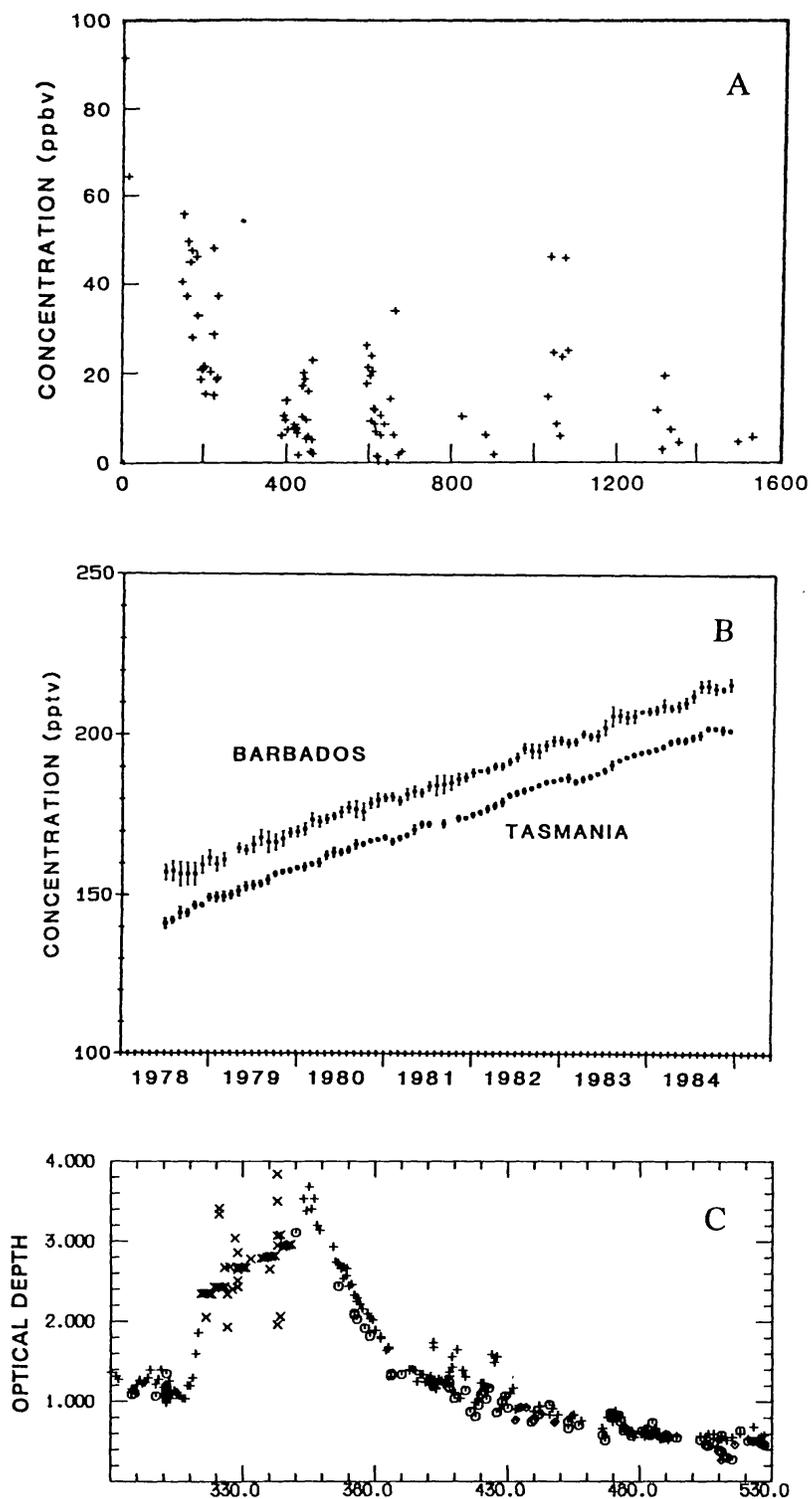
Secondary Origin of the Atmospheres of Venus, Earth, and Mars

One shared characteristic of these three atmospheres is their secondary origin. This was first pointed out for the Earth by several authors (e.g. Brown 1949, Russell & Menzel 1933, Aston 1924), who noted that the rare gases (Ne, Ar, Kr, Xe) are much less abundant than other volatiles on the surface of the Earth. These large depletions are shown in Table 5. The large depletion of Ne to N_2 is particularly striking because Ne and N have very similar solar abundances and similar atomic weights.

Table 5 also shows that the nonradiogenic rare gases are generally more depleted than the chemically reactive volatiles in the atmospheres of Venus and Mars. Several exceptions to this trend are also evident and are discussed later. Nevertheless, the much larger depletions of nonradiogenic ^{20,22}Ne and ^{36,38}Ar compared with the CO_2 and N_2 depletions on all three planets show that the planetary atmospheres did *not* originate principally by capture of gas from the solar nebula. Instead, these atmospheres are almost entirely secondary and originated as the result of chemical processes contemporaneous with or subsequent to the formation of the planets.

One exception to this conclusion may be ^{36}Ar on Venus, which Wetherill (1981) has proposed is due to solar wind implantation in the solid grains accreted by Venus. This hypothesis is attractive because it explains the

Table 5   Depletions of important volatiles in Venus, Earth, and Mars relative to solar abundances [(g/gSi)/(g/gSi)][a]

Volatile	Venus[b]	Earth	Mars
CO_2	3×10^{-5}	3×10^{-5}	2×10^{-8}
H_2O	2×10^{-9}	2×10^{-4}	4×10^{-12}
F	3×10^{-9}	2×10^{-2}	—
^{20,22}Ne	1×10^{-9}	4×10^{-11}	2×10^{-13}
N_2	1×10^{-5}	2×10^{-5}	5×10^{-9}
S	1×10^{-7}	7×10^{-5}	—
Cl	3×10^{-8}	7×10^{-3}	—
^{36,38}Ar	1×10^{-7}	2×10^{-9}	1×10^{-11}
^{84}Kr[c]	$(0.04–1) \times 10^{-5}$	1×10^{-7}	2×10^{-9}
^{132}Xe	—	9×10^{-8}	3×10^{-9}

[a] Solar abundances from Cameron (1982). Atmospheric inventories only were considered for Venus and Mars and were obtained from Tables 3 and 4. Atmospheric plus oceanic plus crustal inventories were considered for Earth and were obtained from Ronov & Yaroshevsky (1976), Turekian (1969), and Ozima & Podosek (1983).
[b] Bulk composition models V2, E5, and Ma2 from the Basaltic Volcanism Study Project (1981, p. 641) were used to determine Si contents for Venus, Earth, and Mars, respectively.
[c] Values for Venus reflect differences between various instrumental measurements. The value for Mars is total Kr; its depletion factor was calculated assuming terrestrial isotopic abundances.

remarkable decrease in ^{36}Ar from Venus to Earth to Mars (see Table 5). However, Wetherill's model and a similar hypothesis advanced by McElroy & Prather (1981) require that radial transport in the inner regions of the solar nebula be sufficiently weak to prevent the ^{36}Ar-rich grains from being mixed in any important amounts out to the accretion zones of Earth and Mars. This requirement argues against a common origin for the grains accreted by Venus and Earth during their formation. We return to this point in connection with the dramatically different H_2O inventories of Venus and Earth.

Finally, we note that models for accretion of the Earth (and by implication Venus and Mars) in the gaseous solar nebula are also inconsistent with the observed inventories of nonradiogenic rare gases on these three planets. In these models the planetary inventories of the nonradiogenic rare gases are established by solubility equilibria between the solar nebula gas and magma oceans on the surfaces of the protoplanets (Mizuno et al 1982). However, major predictions of these models (e.g. a terrestrial Ne inventory 3 to 200 times larger than the atmospheric inventory and with a solar $^{20}Ne/^{22}Ne$ ratio of 14.3 vs the terrestrial value of 9.8) are very difficult to reconcile with the observed rare-gas inventories and isotopic ratios. Comprehensive reviews of constraints imposed upon these models by current knowledge of planetary rare-gas systematics are given by Ozima & Podosek (1983).

Volatile Retention by Solid Grains in the Solar Nebula

Evidently, in order to understand the origin of the atmospheres of Venus, Earth, and Mars we must first understand the chemical processes responsible for retention of volatiles (e.g. H_2O, C, N, F, Cl, S) by the solid grains that accreted to form the planets. We will then be able to address some of the questions posed by Table 5. For example, is the difference between the H_2O inventories of Venus and Earth genetic or evolutionary? If it is genetic, why do the two planets have very similar inventories of CO_2 and N_2? If it is evolutionary, what does the loss of a terrestrial H_2O inventory imply for the chemistry of Venus? Similarly, we would like to know if Mars is really more volatile poor than Earth or only appears to be so. We address these (and related) questions within the framework of currently accepted solar nebula models in which radial temperature gradients are presumed to be a major influence on the composition of the gas and dust grains.

As the interstellar gas and dust were accreted by the solar nebula, they were thermally and chemically equilibrated to varying degrees. Accreting gases may have been only partially equilibrated (or not at all) as they were warmed and compressed. The extent to which this may have occurred depended on the distance of the gas parcel from the proto-Sun and the

rate of radial transport in the nebula relative to the rate of the equilibrating reactions in the gas parcel.

Similar considerations apply to the accreted interstellar dust grains. Recent work (Cameron & Fegley 1982, Morfill & Völk 1984) suggests that the accreting dust grains may have evaporated only partially or not at all, depending on the type of grain, the strength of radial mixing in the nebula, and the distance from the proto-Sun. Indeed, isotopic data for the ancient Ca, Al-rich inclusions in the Allende meteorite imply that these inclusions formed by a complex sequence of condensation, evaporation, and recondensation (Niederer & Papanastassiou 1984). Such observations and theoretical models suggest that evaporation and recondensation leading to thermal and chemical equilibration were very probable in the inner regions of the solar nebula.

However, these arguments become less and less convincing with increasing radial distances (and thus lower temperatures) in the solar nebula. Again, inferences from meteorites are instructive. Observed isotopic anomalies in several light elements in the volatile-rich carbonaceous chondrites (e.g. see the review by Pillinger 1984) imply interstellar material (or at least its chemical and physical signature) is preserved in these meteorites. These caveats should be kept in mind as we discuss the implications of a chemical model of the solar nebula, which assumes complete evaporation and recondensation of the grains and complete chemical equilibration of the gas and dust, for the volatile inventories of Venus, Earth, and Mars.

Table 6 lists the predicted volatile-bearing phases that are stable in this model of the inner region of the solar nebula. Several of these phases are also included in Figure 12, which displays their abundance as a function of temperature and radial distance in the solar nebula. The most important conclusion from these results is that the solid grains equilibrated at lower temperatures (i.e. farther from the proto-Sun) are predicted to be more volatile-rich than the solid grains equilibrated at higher temperatures (i.e. closer to the proto-Sun). However, important exceptions to this behavior are the amounts of elemental carbon and nitrogen, dissolved in Fe-Ni alloy, that go through maxima in the inner region of the nebula (Lewis & Prinn 1984, Fegley 1983).

Table 7 presents a synthesis of the observed volatile inventories for Venus, Earth, and Mars and the predicted volatile inventories of the complete equilibrium model of Table 6 and Figure 12. This comparison provides instructive answers to the questions posed at the beginning of this section. The difference between the H_2O inventories of Venus and Earth is predicted to be genetic. The Earth accreted significantly more hydrated phases (e.g. tremolite, serpentine, hydroxyapatite, talc) than did Venus because these phases only became thermodynamically stable in the

Table 6 Predicted volatile-bearing phases stable at thermochemical equilibrium in solar nebula gas and potential outgassed volatiles[a]

Equilibration temperature (K)[b]	Volatile-bearing phase	Potential volatile(s)[c]
1825	U, Th in Ca-bearing refractories	^{4}He
1520	C,N in Fe-Ni alloy	CO, CO_2, CH_4 N_2, NH_3
1225	Schreibersite $(Fe, Ni)_3P$	P_x, PO_x, PH_3
950–1050	Feldspars and feldspathoids $(Na,K)AlSi_3O_8$, $(Na,K)AlSiO_4$	^{40}Ar
895	Sodalite $(3NaAlSiO_4 \cdot NaCl)$	Cl_2, HCl
766	Fluorapatite $(Ca_5(PO_4)_3F)$	HF
714	Whitlockite $(Ca_3(PO_4)_2)$	P_x, PO_x, PH_3
687	Troilite (FeS)	S_x, H_2S, COS, SO_2
480	Tremolite $(Ca_2Mg_5Si_8O_{22}(OH)_2)$	H_2O, H_2, O_2
460	Hydroxyapatite $(Ca_5(PO_4)_3OH)$	H_2O, H_2, O_2
$\simeq 400$	Talc $((Mg,Fe)_3Si_4O_{10}(OH)_2)$	H_2O, H_2, O_2
$\simeq 400$	Serpentine $((Mg,Fe)_3Si_2O_5(OH)_4)$	H_2O, H_2, O_2
350	Bromapatite $(Ca_5(PO_4)_3Br)$	Br_2, HBr

[a] Complete gas phase, gas-solid, and solid-solid equilibrium assumed. See Barshay (1981), Fegley (1983), and Lewis & Prinn (1984) for details.

[b] Highest temperature at which the phase is stable along the model solar nebula adiabat. The relative sequence does not change with total pressure over very wide ranges.

[c] The exact nature of the potential volatiles depends on several factors including the pressure, temperature, and oxygen fugacity during outgassing. F_2 is so reactive it probably never forms; H_2 and O_2 are generated by equilibria with a H_2O-bearing vapor and with other phases such as Fe metal.

cooler nebular region outside of the Earth's orbit. Furthermore, Mars accreted even more of the hydrated phases than the Earth did and is predicted to be even more H_2O-rich. The (inferred) presence of hydrated silicates on the surface of the asteroid 1 Ceres is in qualitative agreement with this trend (Lebofsky 1978). An alternative model requiring massive H_2O loss from an initially "wet" Venus is discussed in the section on evolutionary processes.

Another prediction is that Venus and Earth formed with initially similar inventories of CO_2, S, Cl, and F, while Mars was initially richer in S, Cl, and F than the Earth but formed with less CO_2. However, Mars may have formed with an Earth-like CO_2 inventory if nonequilibrium effects prevailed, as we show below. Comparison of these predictions with the observed volatile inventories is complicated by atmosphere-lithosphere interactions on both Venus and Mars that may reduce the atmospheric inventories of CO_2, S, Cl, and F. These effects may not be significant for CO_2 on Venus because the atmospheric CO_2 inventory is very similar to the terrestrial bulk inventory (see Tables 5 and 7). However, as Table 3
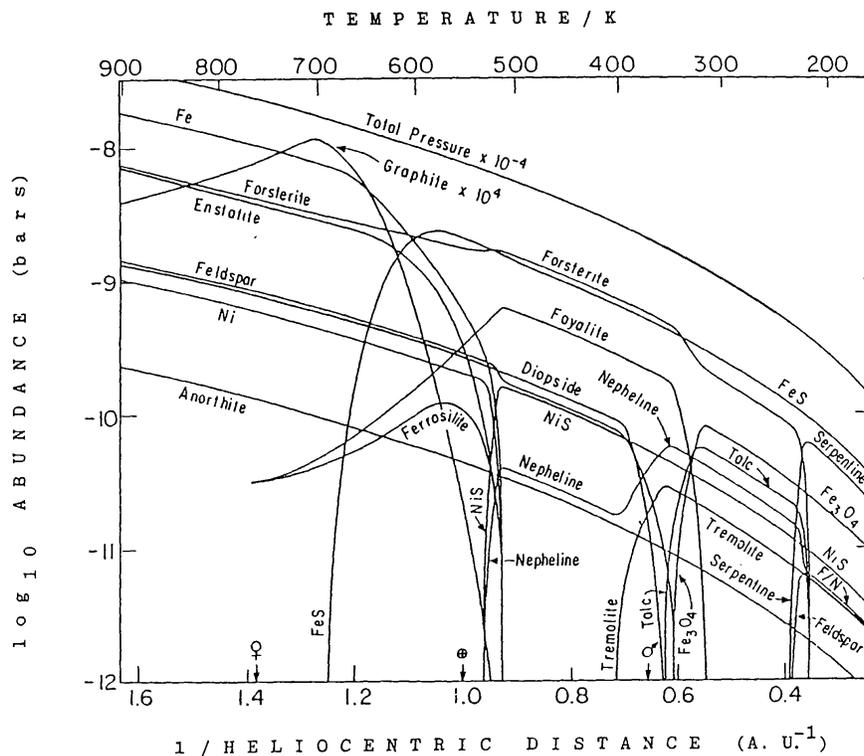
A
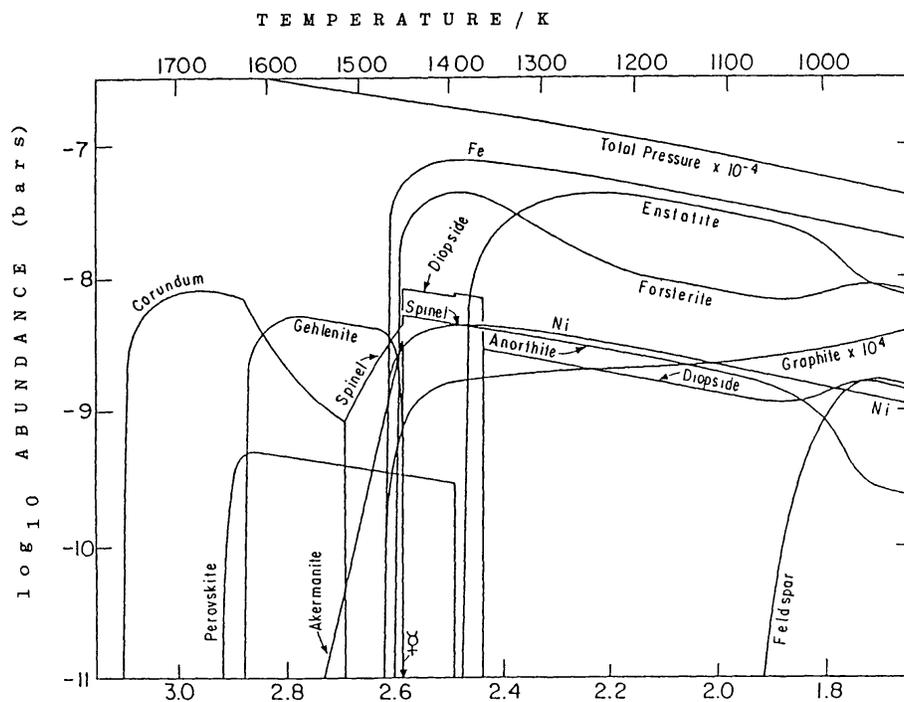
B

Table 7 Comparison (g/g) of observed volatile inventories of Venus, Earth, and Mars with predictions of the complete equilibrium model shown in Figure 12[a]

		Venus		Earth		Mars	
	Volatile	Atmosphere	Bulk	Atmosphere	Bulk	Atmosphere	Bulk
CO_2	(observed)	10^{-4}		4×10^{-10}	8×10^{-5}	4×10^{-8}	
	(predicted)[b]		2×10^{-5}	7×10^{-6} to 3×10^{-4}		10^{-9} to 8×10^{-5}	
N_2	(observed)	2×10^{-6}		6×10^{-7}	3×10^{-6}	7×10^{-10}	
	(predicted)		4×10^{-9}	3×10^{-11}		10^{-13}	
H_2O	(observed)	4×10^{-9}		5×10^{-9}	4×10^{-4}	5×10^{-12}	
	(predicted)		0	10^{-5}		8×10^{-3}	
S	(observed)	10^{-8}	$(4\text{--}6) \times 10^{-3}$	10^{-15}	6×10^{-6}		4×10^{-2}
	(predicted)		10^{-2}	5×10^{-2}		7×10^{-2}	
Cl	(observed)	3×10^{-11}	$<3 \times 10^{-3}$	10^{-15}	6×10^{-6}		8×10^{-3}
	(predicted)		10^{-4}	7×10^{-4}		9×10^{-4}	
F	(observed)	2×10^{-13}		4×10^{-16}	10^{-6}		
	(predicted)[b]		10^{-5}	6×10^{-5}		8×10^{-5}	

[a] Atmospheric inventories based on Tables 2–4. Terrestrial bulk inventory based on Table 5. The S and Cl bulk inventories for Venus and Mars are based on Surkov et al (1984) and Toulmin et al (1977), respectively. In both cases the observed S and Cl contents (or upper limits) are taken as the bulk inventories. Note that this table is not normalized to Si and is simply on a (g/g) basis.

[b] Predictions based on Barshay (1981), Lewis & Prinn (1984), and Fegley (1983). The range of CO_2 values for Earth and Mars includes the effects of kinetic inhibition on dissolved carbon in grains.

indicates, $CaCO_3$ formation is a possible sink for CO_2 in the atmosphere of Venus. By contrast, $CO_2(s)$ in the Martian polar caps is a known CO_2 sink on Mars. Furthermore, S and Cl have been observed on the surface of Mars (Toulmin et al 1977), and S has been observed on the surface of Venus (Surkov et al 1984). The geochemical similarity of F and Cl suggests that F may also be present on the Martian surface, while the (probable) buffering of HCl and HF in the atmosphere of Venus suggests the presence of Cl and F in surface minerals (Lewis 1970).

Finally, two other important trends shown in Table 7 deserve attention. First, both Venus and Earth contain more CO_2 than the complete equilibrium model predicts. Second, Venus, Earth, and Mars all contain substantially more N_2 than predicted. Significantly, a similar situation holds for the chondritic meteorites, especially for the volatile-rich carbonaceous chondrites (Lewis & Prinn 1984, Fegley 1983). The latter meteorites may contain several percent (by mass) of nonequilibrium organic material,

Figure 12 Equilibrium abundances of volatile-bearing phases and major-element condensates along an adiabatic (P, T) profile in the inner regions of the solar nebula. The astrological symbols for Mercury, Venus, Earth, and Mars are shown at the appropriate places on the distance scale, which is in inverse astronomical units (AU^{-1}) (after Barshay 1981).

which is the dominant reservoir of C and N in the meteorites (e.g. see Kung & Clayton 1978). Thus we now explore nonequilibrium effects on volatile retention by solid grains.

Nonequilibrium effects in a cooling parcel of gas and dust in the solar nebula will be favored when the characteristic cooling time (t_{cool}) is less than the characteristic chemical time scales for the gas phase (t_g), gas-solid (t_{gs}), and solid-solid (t_{ss}) reactions that may occur inside this parcel. This is expressed by the inequalities $t_{cool} < t_g$, $t_{cool} < t_{gs}$, and $t_{cool} < t_{ss}$. These inequalities will be favored by low temperatures, fast radial mixing rates, and fast nebular cooling rates; for reactions involving solids, the inequalities will also be favored by large grain sizes and fast accretion rates for these grains. How will nonequilibrium effects influence volatile retention by solid grains?

We can gain some insight into this question by considering three reactions that exemplify volatile retention reactions in a cooling parcel of gas and dust in the solar nebula. First, consider solid-solid reactions, which are likely to be the most sluggish and hence the most susceptible to nonequilibrium effects. The retention of H_2O as the hydrous mineral serpentine (see Table 6) proceeds by the reaction

$$Mg_2SiO_4(s) + MgSiO_3(s) + 2H_2O(g) = Mg_3Si_2O_5(OH)_4(s), \qquad (5)$$
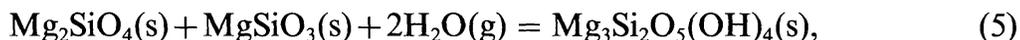
which because it requires the transport and reaction of elements between two minerals, may proceed very slowly at the low temperatures ($\simeq 400$ K) where serpentine is thermodynamically stable in the solar nebula. If this is the case, then $t_{cool} \ll t_{ss}$ may hold, and in the absence of "fast" pathways for forming equal amounts of other hydrated phases, H_2O may not be retained in solid grains until below 200 K, when H_2O (ice) becomes stable. Tremolite and hydroxyapatite, which are stable at higher temperatures, are much less important for H_2O retention because of the significantly lower solar abundances of Ca and P relative to Mg and Si. The implications for H_2O retention by Venus, Earth, and Mars are twofold. First, H_2O must then be delivered to these planets by icy planetesimals gravitationally scattered into the inner solar system during the late stages of planetary accretion (e.g. Wetherill 1975). Then Venus and Earth would be predicted to have similar initial H_2O inventories. Second, we would then require a mechanism to remove the equivalent of the Earth's oceans from Venus in order to explain its present H_2O-depleted state.

An exemplary gas-solid reaction, the formation of troilite, proceeds by H_2S permeation into and reaction with Fe metal grains:

$$Fe(s) + H_2S(g) = FeS(s) + H_2(g). \qquad (6)$$

Given sufficiently rapid radial mixing or nebular cooling, then $t_{cool} \ll t_{gs}$

may hold and this reaction may not proceed significantly before being quenched at some intermediate conversion of H_2S to troilite (FeS). Although a few percent of the H_2S may be retained as an alkali sulfide at similar temperatures (Lewis & Prinn 1984), the bulk of the available S cannot be retained in solid grains until below 200 K, when $NH_4HS(s)$ or $H_2S(s)$ forms (Lewis & Prinn 1984). Again, the major implication is that planetesimals formed in the outer solar system must impact Venus, Earth, and Mars to provide these planets' observed sulfur inventories.

Finally, let us consider a gas phase reaction such as the conversion of CO to CH_4:

$$CO(g) + 3H_2(g) = CH_4(g) + H_2O(g). \tag{7}$$
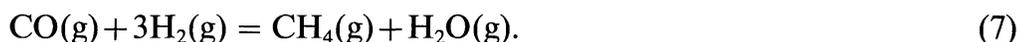
The kinetic inhibition of the CO to CH_4 conversion has in fact been studied quantitatively (reviewed in Lewis & Prinn 1984). The presence of metastable $CO(g)$ inside the $CH_4(g)$ stability field leads to supersaturation of elemental carbon in the gas phase. Figure 13, which compares the equilibrium and nonequilibrium cases for reaction (7), illustrates that one consequence of this situation may be greatly increased amounts of carbon dissolved in Fe-Ni alloy equilibrated with this gas. The range of predicted CO_2 inventories given in Table 7 for Earth and Mars incorporates this enhancement. In this instance, nonequilibrium effects increase the ease of volatile retention by solid grains in the inner regions of the nebula.

Another possible consequence of the kinetic inhibition of the CO to CH_4 conversion is that reactions in the supersaturated carbon-bearing gas will proceed to the point of making organic material, as in the Fischer-Tropsch reactions studied by Anders and coworkers (Hayatsu & Anders 1981). Large Martian CO_2 inventories are also plausible in this case. In fact, such nonequilibrium organic matter may have been an important source of the CO_2 and N_2 in the atmospheres of Venus, Earth, and Mars.

Volatile Degassing and Atmospheric Formation

We now have some insight into the chemical and physical processes responsible for influencing volatile retention by solid grains in the solar nebula. Once these grains are incorporated into Venus, Earth, and Mars, their volatiles are released (to varying degrees) by degassing and atmospheric formation occurs. How can our knowledge of the atmospheres of Venus, Earth, and Mars help us to develop models of this complex process? What factors are responsible for influencing the amount and initial composition of the degassed volatiles? Again, we address these questions by emphasizing the roles of common chemical and physical processes acting on all three planets. More detailed models that are specific for the Earth have
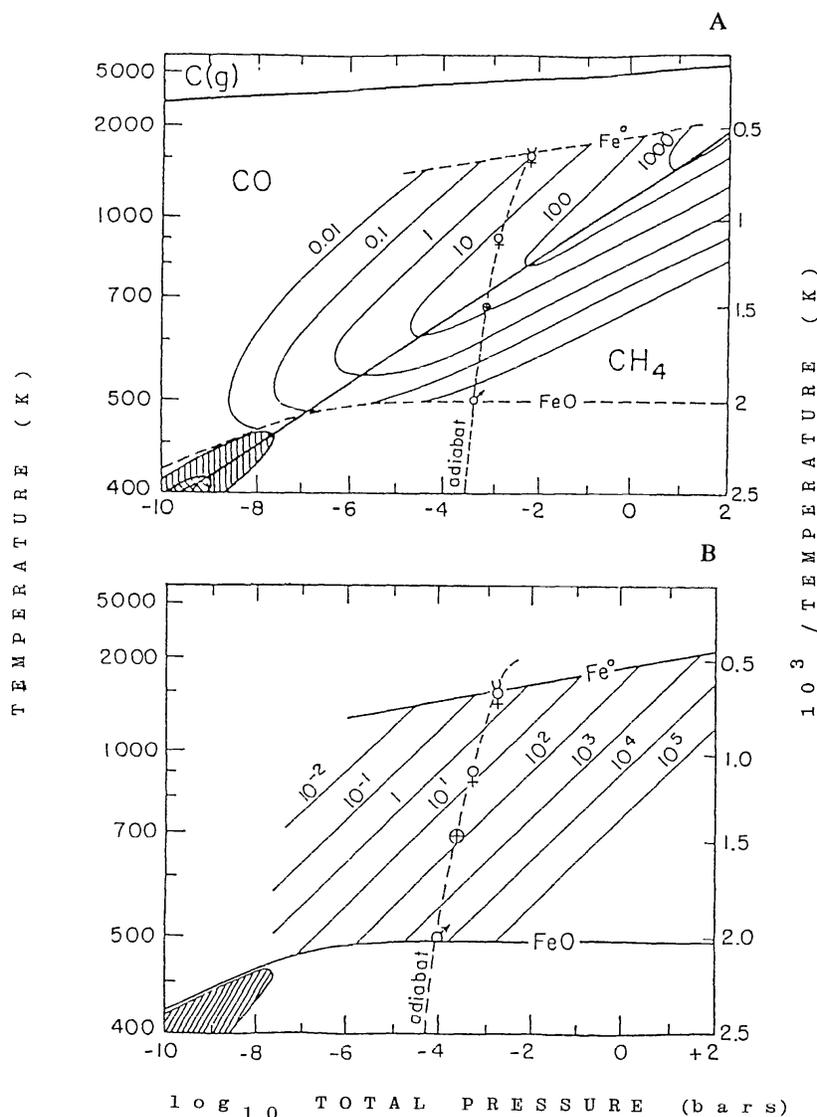
Figure 13   Calculated amounts (parts per million by mass) of elemental carbon dissolved in Fe-Ni alloy equilibrated with nebular gas. The (P, T) adiabat from Figure 12 is also shown. (*A*) Complete equilibrium case; (*B*) kinetic inhibition of the CO to CH_4 conversion (after Lewis & Prinn 1984).

been reviewed by Ozima & Podosek (1983), Holland (1984), and Lewis & Prinn (1984).

Volatile degassing will occur when the equilibrium vapor pressure of a volatile species over its condensed phase exceeds the pressure due to the overlying materials. This situation is favored by high temperatures and low pressures. Several potential heat sources are available during the formation and early history of Venus, Earth, and Mars. These include (*a*) heating during planetary accretion, (*b*) heating by strong coupling of a

planetary body with the T-Tauri solar wind, (c) heating by short-lived radionuclides such as ^{26}Al, (d) heating by long-lived radionuclides such as ^{40}K, ^{232}Th, ^{235}U, and ^{238}U, and (e) heating during planetary differentiation and core formation. Several of these processes, such as accretion heating, heating from long-lived radionuclides, and heating from planetary differentiation, are currently thought to have been the most important processes for Venus, Earth, and Mars. Thus, since the accretion rates, radionuclide abundances, and degrees of differentiation may have been very different for these three planets, the times and rates of volatile degassing may also have varied significantly. In particular, the smaller size of Mars relative to Venus and Earth suggests that accretion heating may not have been as great for Mars. Thus, Mars may be less efficiently degassed than Venus or Earth.

Furthermore, the differing compositions of these three planets may have also influenced the composition and oxidation state of degassed volatiles. Thus, if Venus was initially H_2O poor, the degassed volatiles would reflect this and would be dominated by C-, N-, and S-bearing gases rather than by H_2O. In fact, calculations by Gerlach & Nordlie (1975) clearly show an increase in C- and S-bearing gases (N was excluded from their calculations) as H_2O drops off. The latter volatile is generally the dominant constituent of present-day volcanic gases on the Earth (e.g. see Gerlach & Nordlie 1975).

Likewise, the equilibrium models suggest that degassed volatiles on Mars may also have been initially H_2O rich. The (inferred) presence of abundant H_2O on Mars (see the review in Lewis & Prinn 1984) is in qualitative agreement with this prediction.

The oxidation state of the degassed volatiles on Venus, Earth, and Mars may also have been initially different as a consequence of the solid grains accreted by each planet equilibrating with the nebular gas at different temperatures (see Figure 12). The shifting equilibrium with temperature between H_2 and H_2O in the gas phase controls the oxygen fugacity (fO_2) of the gas and dust grains in equilibrium with it. In this case the solid grains become more oxidized (e.g. more FeO rich) with decreasing temperature (i.e. increasing radial distance) in the nebula. The (initially) degassed volatiles on Venus, Earth, and Mars would then follow the same trend. However, if the time scale (t_{gs}) for the relevant gas-solid reactions controlling the fO_2 of the solid grains is sufficiently large relative to the characteristic cooling time scale (t_{cool}) defined earlier, then the fO_2 of the solid grains may be frozen in (or quenched) at a sufficiently high temperature $T = T_Q$, which may be the same for all three planets. In this case, the initially degassed volatiles may have had the same oxidation state on all three planets. At present we are unable to distinguish between these

two (extreme) possibilities. This situation is partly due to our lack of information on the composition of volatiles initially outgassed on any of these three planets and partly due to our present ignorance of the quench temperatures of the relevant reactions in the solar nebula. However, while information on the former topic is unlikely to become available anytime soon, information on the latter could be provided by suitably designed theoretical models of nebular chemistry.

Similar considerations are also relevant for volatile degassing on the three planets. Figure 14 illustrates several possible paths (e.g. volcanism, evaporation, sublimation, slow upward permeation, effusion) that may be involved to different degrees (and at different times) in volatile degassing. Some degassing mechanisms, such as mineral devolatilization at depth, may be coupled with subsequent reactions with gaseous, liquid, or solid phases that will change the composition and oxidation state of the volatile phase. By analogy with our treatment of nebular reactions, it is convenient to define characteristic chemical lifetimes for the gas phase (t_g), gas-magma (t_{gm}), and gas-rock (t_{gr}) reactions involved in degassing. It is also convenient to define a characteristic time scale (t_{trans}) for the upward transport of the volatile phase and a critical depth D^* where $t_{chem} = t_{trans}$. Here we take $t_{chem} = t_g$, t_{gm}, or t_{gr} as appropriate for the type of reaction being considered. Thus we see that the relevant reactions will only be effective for changing the composition and oxidation state of the volatile phase at depths $D > D^*$, where $t_{chem} < t_{trans}$. Conversely, the gas phase, gas-magma, and gas-rock reactions will be ineffective for altering the volatile phase at depths $D < D^*$, where $t_{chem} > t_{trans}$. At depths $D = D^*$ ($t_{chem} = t_{trans}$) quenching of the relevant reaction will occur, and the composition and fO_2 of the ascending volatile phase will also be frozen in.

In general, the chemical time scales will decrease rapidly with increasing depth in the planet. The critical depth D^* will be different for each reaction considered because of the different chemical time scales. Just as importantly, D^* will vary with the mode of degassing because of the inherent variations in the time scales for upward transport of the volatile phase. For example, reactions occurring in a volatile phase slowly permeating through a layer of rock will quench closer to the surface than reactions in a volatile phase carried to the planetary surface by a volcanic eruption.

Such constraints are potentially very important for defining the composition and fO_2 of degassed volatiles. A simple example based on the calculations of Heald et al (1963) for the equilibrium abundances in a terrestrial volcanic gas illustrates this point. If the gas phase were quenched at 1400 K, the resulting CO/CH_4 molecular ratio would be $10^{9.9}$, while the same gas quenched at 400 K would have a CO/CH_4 molecular ratio of only $10^{-4.4}$. We also note that Fe metal grains will directly influence the
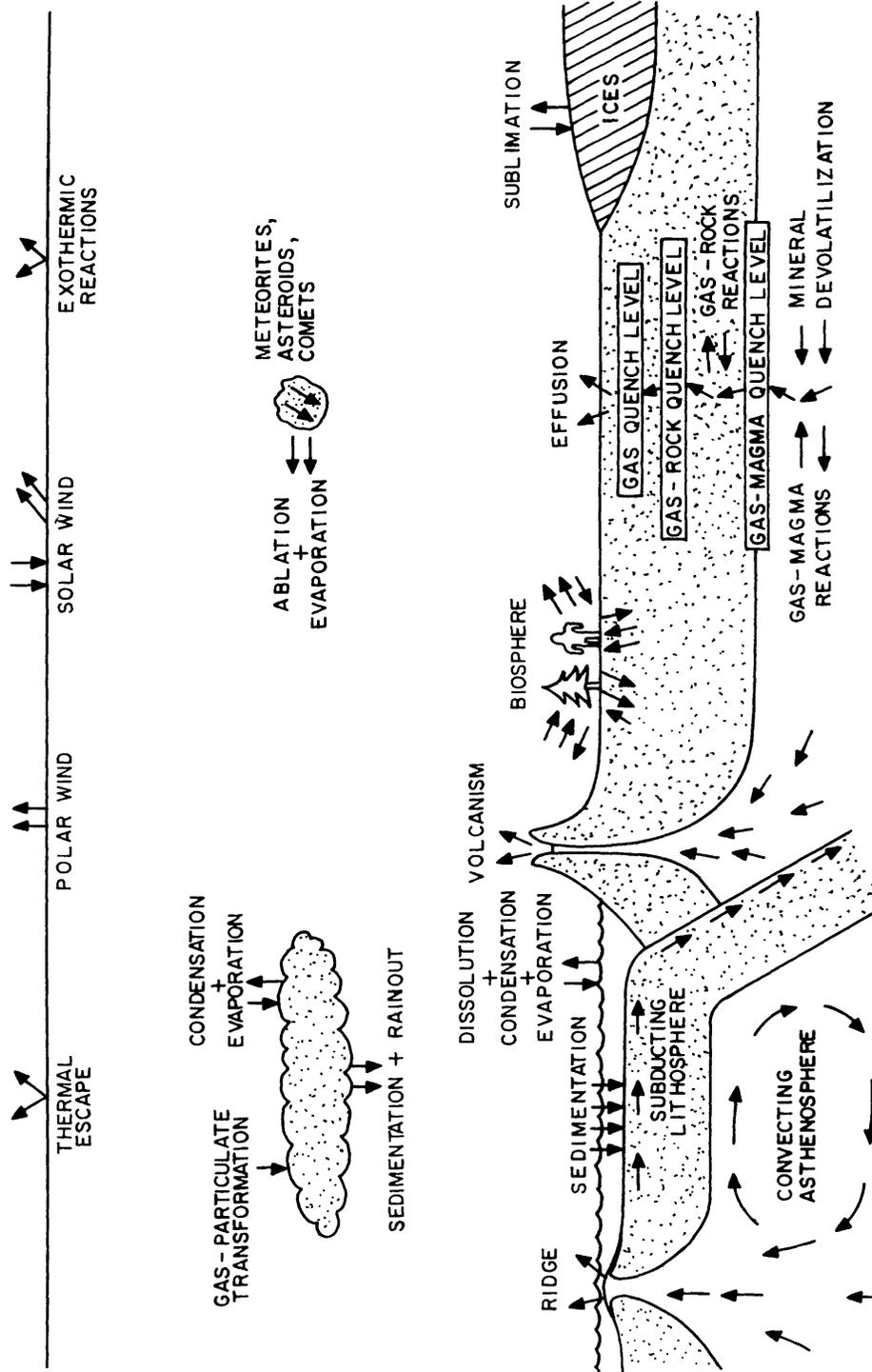
Figure 14 Schematic diagram illustrating the processes affecting volatiles in planetary atmospheres. Net fluxes are illustrated by arrows (after Prinn 1982).

fO_2 of the volatile phase (e.g. see Holland 1984) and will also act as a catalyst for conversions of $CO + CO_2$ to CH_4, N_2 to NH_3, etc, and thus influence the quench levels of gas phase reactions. More work is clearly required in this area of kinetic constraints on the degassing process.

Finally, we note that relative to the total planetary mass the present atmospheric inventories of ^{40}Ar on Venus, Earth, and Mars are 3×10^{-9}, 11×10^{-9}, and 0.6×10^{-9} (g/g), respectively. These inventories imply similar degassing efficiencies for Venus and Earth and an order of magnitude lower degassing efficiency for Mars. This trend is consistent with (but does not prove) the hypothesis that Mars is volatile rich and only appears volatile poor because the volatiles are sequestered in the interior.

Evolutionary Processes, Sources, Cycles, and Sinks

After volatiles are present in a planetary atmosphere, they are subject to a variety of competing influences that may affect them in several ways (see Figure 14). Several of these influences, such as thermal escape, interactions with electromagnetic fields in polar regions (i.e. polar wind), interactions with the solar wind, and exothermic reactions, cause loss of the volatiles to space. Other influences, such as solar ultraviolet radiation and high temperatures (e.g. possibly generated by lightning or by shock heating from impacting bolides), lead to chemical conversions and reprocessing. The synthesis and destruction of volatiles by living organisms also lead to chemical transformations and are unique to the Earth. A variety of exchange and weathering reactions between the atmosphere and lithosphere (and hydrosphere on Earth) further serve to cycle and modulate the atmosphere's composition and overall inventory of various degassed species. Instead of reviewing all these processes, we discuss here an episodic phenomenon (large cometary and asteroidal impacts into planetary atmospheres) and a chronic phenomenon [the (inferred) loss of H_2O from an initially "wet" Venus] that exemplify the differing influences of these two classes of processes on atmospheric evolution.

LARGE ASTEROIDAL AND COMETARY IMPACTS   Several recent studies have shown that large bolide impacts may have affected the Earth throughout its history. Planetesimal impacts during and shortly after the accretion of the Earth may have formed the Moon (Cameron & Ward 1976) and have released atmospheric gases by impact devolatilization (Lange & Ahrens 1982). Large impacts, especially on Mars, may also have been a mechanism for atmospheric erosion and blowoff (Cameron 1983). A late heavy bombardment (Wetherill 1975) may also have caused chemical reprocessing of the Earth's early atmosphere (Fegley et al 1986). Significantly later in the Earth's history, the impact of an $\simeq 10$-km bolide may have terminated the

Cretaceous era (Alvarez et al 1980), leading to severe environmental effects and biospheric disruptions (Lewis et al 1982, Prinn & Fegley 1986). Finally, in recent times the 1908 impact event at Tunguska, Siberia, led to global perturbations in atmospheric ozone (Turco et al 1981), severe environmental effects in the immediate vicinity of the endpoint of the trajectory, and atmospheric pressure waves recorded across Russia and Europe (Shoemaker 1983).

Shoemaker (1983) reviews estimates of the energy released by the 1908 Tunguska impact. These estimates are in the range of 12–30 megatons TNT equivalent. He further estimates the frequency of such encounters with the Earth as once every $\simeq 10^{2.5 \pm 0.3}$ yr (12 megatons) and once every $\simeq 10^{2.8 \pm 0.3}$ yr (30 megatons). Shoemaker's (1983) estimated mean frequency of encounters with $\simeq 10$-km impactors, such as the putative Cretaceous-Tertiary impactor 65 Myr ago, is about once every 10^8 yr. This frequency is small but still impressive on a geological time scale. It is therefore instructive to review the atmospheric effects of large asteroidal and cometary impacts.

Large bolides ($\simeq 10$ km size) impacting a planet will cause severe shock heating and chemical reprocessing of the planetary atmosphere during atmospheric entry and as a result of the supersonic plume ejected on impact (Prinn & Fegley 1986). The nature of the products of this shock heating and chemical reprocessing depend on the oxidation state of the planetary atmosphere. Nitrogen-bearing shock products are particularly interesting because of their potential environmental effects. NO is produced in oxidizing atmospheres (atomic C/O < 1), while HCN is produced in reducing atmospheres (atomic C/O $\geq$ 1) (Fegley et al 1986). The former case is relevant to the present atmospheres of the Earth, Venus, and Mars, while the latter case is relevant to (postulated) primitive atmospheric compositions on the Earth. The scope of the chemical and physical consequences of the impacts also depends on the nature of the impactor, although these consequences are likely to be very severe in all cases.

Detailed studies (Lewis et al 1982, Prinn & Fegley 1986, Fegley et al 1986) illustrate some potential environmental effects of such large impacts. These may extend to the atmosphere, lithosphere, hydrosphere, and biosphere. For example, if the putative Cretaceous-Tertiary impactor were cometary, it would produce semiglobal atmospheric NO_2 volume mixing ratios of 0.1% and concentrated nitrous and nitric acid rain with a pH $\simeq$ 0–1.5 globally (Prinn & Fegley 1986). The resulting consequences may include (*a*) inhibition of photosynthesis due to extinction of solar radiation by NO_2, (*b*) foliage damage due to exposure to NO_2 and HNO_3, (*c*) toxicosis resulting from massive mobilization of soil trace metals, (*d*) respiratory damage due to exposure to NO_2, (*e*) decreases in the pH of the oceanic

mixed layer, (f) global warming due to this sudden CO_2 injection into the atmosphere, (g) extinction of many calcareous-shelled organisms, and so on (Prinn & Fegley 1986). Similarly, impacts into reducing atmospheres postulated for the primitive Earth may lead to production of large amounts of HCN, an important precursor for the abiotic synthesis of complex organic molecules (Fegley et al 1986). Thus, although episodic in character, asteroidal and cometary impacts may have had a significance for atmospheric evolution far beyond their potential role as suppliers of volatiles.

LOSS OF WATER FROM AN INITIALLY "WET" VENUS   The proposed loss of water from an initially "wet" Venus exemplifies the type of chronic phenomena that have influenced atmospheric evolution. If the initial volatile endowments of the Earth and Venus were not controlled by the radial temperature gradient in the solar nebula, then both Venus and Earth may have formed with similar H_2O inventories. Thus the greater proximity of Venus to the Sun may have led to a H_2O-rich atmosphere with a steadily increasing atmospheric opacity (the so-called runaway greenhouse). The H_2O is then irreversibly dissociated to H_2 and O, with loss of these species. The H_2 is lost by escape to space, and the O is lost either by escape or by reactions with the Venusian surface. The end result of these processes is the present "dry" Venus.

This hypothesis has recently received support from the D/H ratio of $\simeq 1.6 \times 10^{-2}$ measured by the Pioneer Venus mass spectrometer (Donahue et al 1982). This value is significantly higher than the terrestrial value of 5×10^{-5} and is consistent with the depletion of an 8–9-m-thick layer of H_2O from Venus over geologic time (McElroy et al 1982, Donahue et al 1982). This amount of H_2O is $\simeq 0.3\%$ of the amount of H_2O on Earth and implies an initially "damp" Venus that had managed to accrete some hydrated minerals, but still not nearly as much as the Earth. However, Donahue et al (1982) also note that for H_2O volume mixing ratios $\geq 2 \times 10^{-2}$, the loss of hydrogen to space involves an upward fluid hydrodynamic flow in which H and D are equally depleted. Thus, enhancement of the D/H ratio can only begin once the H_2O volume mixing ratio drops below $\simeq 2 \times 10^{-2}$, which is equivalent to the 8–9-m-thick layer of H_2O mentioned above.

However, other constraints may help us to distinguish between the "dry," "damp," and "wet" Venus scenarios. For example, what is the fate of oxygen in the latter two cases? This depends to some extent on the oxidation state of the volatile-bearing phases responsible for bringing carbon to Venus. If carbon arrived in a reduced form, either as elemental carbon dissolved in Fe-Ni alloy (as equilibrium considerations predict) or as nonequilibrium organic matter, then it must react with O_2 to produce

the present CO_2-rich atmosphere. If this O_2 was produced from H_2O dissociation, then the present CO_2 inventory on Venus implies a past sink for $\simeq 900$ m of H_2O on a "wet" primordial Venus.

On the other hand, reaction with Fe-bearing phases in the interior of Venus may have provided an O_2 sink. Again, this mechanism depends to some extent on the oxidation state of the solid grains accreted by Venus [e.g. their Fe(metal), Fe^{2+}, and Fe^{3+} ratios] and on the thermal history and differentiation of Venus. However, the reaction of the oxygen contained in a "wet" (Earth-like) Venus requires oxidation of $\simeq 5 \times 10^{24}$ g of Fe to FeO or of $\simeq 2 \times 10^{25}$ g of FeO to Fe_3O_4. This sink then requires reaction of 1–4% of the mass of Venus [for a planet with 10% (by mass) of Fe or FeO] in order to remove the required amount of oxygen. This appears to require a very efficient mechanism for exposing the interior of Venus to the atmosphere.

Finally, we note that the solar wind irradiation models (Wetherill 1981, McElroy & Prather 1981) discussed earlier can provide constraints relevant to H_2O retention by Venus. These models require weak radial transport in the accretion regions of Venus and Earth to preserve the segregation of [36]Ar-rich grains presumably accreted by Venus. Suitably designed theoretical models may therefore be useful for exploring mutually compatible [36]Ar and H_2O inventories (assuming some radial temperature gradient influence on solid grain composition) on Earth and Venus.

CONCLUDING REMARKS

Intensive investigations of our own atmosphere in recent years coupled with Earth-based, satellite, probe, and lander observations of our two nearest planetary neighbors have allowed us to critically compare and contrast the remarkable atmospheres on these three terrestrial planets. This exercise in comparative planetology has provided valuable insight into atmospheric origin and circulation and the biogeochemical processes that control atmospheric composition. We have been able to investigate the common aspects of the meteorology, chemistry, and evolution of the atmospheres of Venus, Earth, and Mars and puzzle over the unique aspects of each atmosphere, exemplified by the remarkable role of the biota in determining and altering the Earth's atmospheric chemical state. As more data are gathered on these three planets, there seems little doubt that such comparisons and contrasts will continue to be stimulating, provocative, and fruitful.

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