

Atmospheric evolution on Venus

Bruce Fegley, Jr.

Planetary Chemistry Laboratory

Department of Earth & Planetary Sciences,

Washington University CB1169,

St. Louis, MO 63130-2302 USA

Tel: +1-314-935-4852

FAX: +1-314-935-4853

e-mail: bfegley@levee.wustl.edu

Submitted to

The Encyclopedia of Paleoclimatology and Ancient Environments

Edited by Vivien Gornitz

January 2004

ATMOSPHERIC EVOLUTION ON VENUS

Overview

Venus and Earth are generally regarded as sister planets because Venus is the planet with mass, size, and mean density closest to that of the Earth (see Table V1). Cosmochemical and geochemical models also suggest that Venus' bulk composition is similar to that of the Earth (Tables 5.8 and 5.9 of Lodders and Fegley, 1998). Despite these broad similarities, Venus' atmosphere is dramatically different from that of the Earth. These differences are primarily due to Venus' depletion in water relative to the Earth. As discussed below, Venus may either have formed "dry", or may have formed "wet" and subsequently lost most of its water. A choice between these two alternatives is impossible at present and there are arguments for and against both models (Lewis and Prinn, 1984; Yung and DeMore, 1999).

Atmospheric evolution on Venus has probably been different than the evolution of the terrestrial atmosphere. However, before discussing this somewhat speculative topic it makes sense to review basic properties of Venus' atmosphere, and to compare its atmosphere to that of the Earth. This article is based on Fegley (2004), Prinn and Fegley (1987), and Warneck (1988). Readers seeking more information about Venus should consult the following sources. *The Encyclopedia of Planetary Sciences* (Shirley and Fairbridge 1997) has several articles about Venus' atmosphere, geology, and geophysics. Brief reviews are given by Fegley (2004) and Lodders and Fegley (1998). Book-length treatments of results from Soviet missions are given by Barsukov et al. (1992), of Pioneer Venus results by Hunten et al. (1983), of Magellan results by Bougher et al. (1997), and atmospheric chemistry on Venus and Mars by Krasnopolsky (1986). Three recommended monographs about different aspects of the chemistry and physics of planetary atmospheres are Chamberlain and Hunten (1987), Lewis and Prinn (1984), and Yung and DeMore (1999).

Venus' Present Day Atmosphere

Venus' atmosphere is mainly CO₂ (96.5% by volume) and N₂ (3.5%) with smaller amounts of noble gases (He, Ne, Ar, Kr, Xe) and chemically reactive trace gases (SO₂, H₂O, CO, OCS, H₂S, HCl, SO, HF, and elemental sulfur vapor). The average temperature and pressure at Venus' surface are 740 K and 95.6 bars at the modal radius (6051.4 km). The temperature gradient throughout Venus' troposphere (0-60 km altitude)

is very close to the dry adiabatic gradient for a mixture of CO₂ (96.5%) + N₂ (3.5%). A global cloud layer composed of aqueous sulfuric acid droplets (H₂SO₄·2 H₂O) at ~45 to ~70 km altitude continuously shrouds Venus' surface from our view. The clouds also play a key role in Venus' current climate. They reflect about 75% of incident solar radiation back to space. Thus Venus absorbs only ~66% as much solar energy (160 W m⁻²) as Earth (243 W m⁻²) even though the incident solar radiation is ~1.9 times larger than at Earth. In addition, ~70% of the sunlight absorbed by Venus is deposited in the upper atmosphere and clouds, in sharp contrast to Earth where ~66% of solar energy is absorbed at the surface. A cloud-free Venus would have a much different climate than Venus does today.

The abundances of CO₂, N₂ and the noble gases are apparently constant throughout much of Venus' atmosphere (0-100 km). However, many trace gas abundances vary with altitude, time, and location. These variations are due to photochemical reactions (including photochemical oxidation of SO₂ to aqueous sulfuric acid cloud droplets) that primarily occur in the upper atmosphere and clouds, and to thermochemical reactions that primarily occur in the hot, dense atmosphere below the clouds. Surprisingly, the *Pioneer Venus* gas chromatograph reported an altitude-dependent N₂ abundance below the clouds in the 22–52 km region (see below). Microwave spectroscopy from Earth, the *Pioneer Venus*, and *Magellan* spacecraft indicates that H₂SO₄ vapor is present below the clouds with an abundance of about 12 parts per million by volume (ppmv). Sulfur trioxide vapor, which has not yet been observed, is expected to be present below the cloud layer in equilibrium with H₂SO₄ gas and water vapor. Both H₂SO₄ and SO₃ have several infrared (IR) absorption bands in the 2-20 μm region and are potentially important greenhouse gases, although at larger concentrations than probably exist in Venus' atmosphere today. Photochemical models predict potentially observable amounts of Cl, Cl₂, ClO, and O₂ in Venus' upper atmosphere (Yung and DeMore, 1999). Tables V1 and V2 summarize chemical and physical data about Venus' atmosphere.

The large abundance of CO₂ in Venus' atmosphere is equivalent to a global layer of calcium carbonate (CaCO₃) 0.88 km thick. This is about twice Earth's crustal carbon inventory which corresponds to a global CaCO₃ layer 0.44 km thick. Volcanic outgassing is probably the major CO₂ source on Venus. The two major CO₂ sinks are solar UV photolysis to CO and O₂ in the upper atmosphere and carbonate formation on Venus' surface. The latter sink is exemplified by the Urey reaction



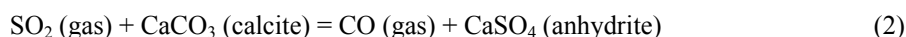
but other carbonates and carbonate-bearing minerals such as scapolite may also be involved. (Scapolite is a solid solution between marialite $\text{Na}_4[\text{Al}_3\text{Si}_9\text{O}_{24}]\text{Cl}$ and meionite $\text{Ca}_4[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{CO}_3$. Sulfate and OH anions may also substitute for the chloride and carbonate anions.)

Several arguments suggest that Venus' surface and interior contain carbonates. Degassing of ^{40}Ar on Venus is incomplete and the atmosphere contains only $24\pm 10\%$ of the ^{40}Ar from radioactive decay (Kaula, 1999). The argon data imply that degassing of CO_2 is also incomplete because argon is degassed easier than CO_2 (Ar is less soluble in silicate melts than is CO_2). Mass deficits in elemental analyses made by X-ray fluorescence (XRF) spectroscopy at the *Venera 13*, *Venera 14*, and *Vega 2* landing sites can be attributed to carbonates, as done with the *Viking* XRF data for Mars. Calculated carbonate abundances are about 4–10% CaCO_3 (Kargel et al., 1994). Geochemical interpretations of the elemental analyses suggest that Venus' mantle contains more CO_2 than the terrestrial mantle (Kargel et al., 1993). Finally, some flow features in *Magellan* radar images may result from carbonatite magmas that have water-like rheologies.

The N_2 abundance in Venus' atmosphere is $3.5\pm 0.8\%$ (see Table V2). Consequently the CO_2 abundance is also uncertain by $\pm 0.8\%$. The uncertainty reflects disagreements between N_2 abundances measured by mass spectrometers on *Pioneer Venus* and *Venera 11-12* and gas chromatographs on the same spacecraft. Volcanic outgassing is probably the major N_2 source on Venus and the formation of nitrogen oxides (NO_x) by lightning may be a N_2 sink. The chemical lifetime of N_2 in Venus' atmosphere is possibly very long ($\sim 10^9$ years). In any case, the apparent dependence of the N_2 abundance on altitude is hard to understand and new measurements are required to resolve this issue.

Sulfur dioxide is the major sulfur gas in Venus' atmosphere, the third most abundant gas overall, and one of the three most important greenhouse gases. It is intimately involved in the formation of the global sulfuric acid clouds, the energy budget and greenhouse effect in Venus' lower atmosphere, and atmosphere-lithosphere interactions such as volcanism and chemical weathering. *In situ* and Earth-based measurements of the SO_2 abundance in Venus' lower atmosphere give an average abundance of about 150 ppmv (22–42 km), which decreases at higher and lower altitudes (Krasnopolsky 1986; Bézard et al. 1993). At higher altitudes photochemical oxidation converts SO_2 into aqueous sulfuric acid cloud droplets and efficiently removes it from Venus' upper atmosphere, which contains about 15,000 times less SO_2 (10 ppbv above the clouds vs. 150 ppmv below them). At lower altitudes gas phase thermochemistry reduces SO_2 to

OCS. On a longer timescale of ~1.9 million years, thermochemical reactions with CaO-bearing minerals on Venus' surface convert SO₂ into anhydrite (CaSO₄)



irreversibly removing SO₂ and the sulfuric acid clouds formed from it. The SO₂ lost from the atmosphere must be replenished by volcanism to maintain the global cloud cover. We return to this topic when we discuss volcanic outgassing and climate change.

Water vapor has an average abundance of about 30 ppmv below Venus' clouds. It is even less abundant above the clouds where only a few parts per million of water vapor are observed. Water reacts with H₂SO₄ to form hydronium (H₃O⁺) and bisulfate (HSO₄⁻) ions. Thus the concentration of "free" H₂O in concentrated sulfuric acid is very small. As a result, the H₂O partial pressure over the cloud droplets is less than that over water ice at the same temperature. The atmospheric H₂O abundance varies spatially and temporally (above and below the clouds). Although a trace gas, H₂O is the major hydrogen reservoir in Venus' atmosphere and is one of the three most important greenhouse gases. It is also involved in gas-solid reactions that regulate, or buffer, atmospheric HCl and HF. These reactions apparently equilibrate rapidly because HCl and HF concentrations above the clouds are the same, within error, as those below the clouds measured about 20 years later. Over a much longer time scale (10⁸–10⁹ years) water loss via H escape to space and oxidation of ferrous iron minerals in Venus' lithosphere regulate the oxidation state of Venus' atmosphere and surface. Volcanism and possibly cometary impacts replenish atmospheric water vapor. The H₂O abundance in Venus' atmosphere is equivalent to a global layer of water one cm thick. However, liquid water is unstable on Venus' hot surface. We consider the isotopic composition of Venusian water when we discuss atmospheric evolution.

The strong infrared nightglow of O₂ at 1.27 μm and the Herzberg II nightglow at 400-800 nm show that molecular oxygen is a trace species in the 100-130 km region of Venus's upper atmosphere (Krasnopolsky 1986). The spectroscopic upper limit for O₂ in Venus' lower atmosphere below ~100 km is less than 0.3 ppmv. For comparison, the Martian atmosphere contains 1300 ppmv O₂, which is also produced by solar UV photolysis of CO₂. The extremely small O₂ abundance on Venus shows that the catalytic recombination of O + CO produced by solar UV photolysis of CO₂ is very efficient because the O₂

abundance is at least 4,300 times smaller than on Mars although the solar flux is about four times larger than on Mars. Yung and DeMore (1999) describe the CO₂ photochemical cycles on Mars and Venus.

Comparisons to Earth's Atmosphere

Earth is an interesting and informative contrast to Venus. Oxygen makes up about 21% of dry air in Earth's atmosphere, with the balance being mainly N₂ (78%), Ar (9340 ppmv), and CO₂ (360 ppmv). The average surface temperature and pressure at sea level are 288 K and one atmosphere. The temperature gradient in the terrestrial troposphere (0–12 km) is an average of the dry and wet adiabatic gradients. Earth is about 50% covered by water clouds at any time. The H₂O abundance in the troposphere ranges from 1–4% and is highest near the equator and lowest near the poles. The H₂O concentration in tropospheric air decreases with altitude and roughly corresponds to 50% relative humidity at any level. The stratosphere contains much less water than the troposphere, about 2–7 ppmv. This is about the same as expected (5 ppmv) from the vapor pressure over water ice at 195 K, the temperature of the tropical tropopause. Some stratospheric water is mixed upward through the tropical tropopause while the rest is produced from CH₄ oxidation by OH radicals. Most of the water at Earth's surface is in the oceans, which are equivalent to a global layer about 2.7 km thick. There is about 270,000 times as much observable water on Earth as on Venus.

In contrast to Venus (and Mars), CO₂ is a trace gas in Earth's atmosphere with an abundance of ~360 ppmv. About 25% of this is anthropogenic and biological sources account for most of the rest. Volcanism is only a minor source of CO₂ in Earth's atmosphere. Most of the carbon at Earth's surface is in the crust (6×10^{19} kg), with carbonates making up 80% of this and organic carbon the remainder. Earth's crustal carbon reservoir is much larger than the oceanic (3.8×10^{16} kg), biospheric (3.7×10^{15} kg), or atmospheric (7.6×10^{14} kg) reservoirs.

Several of the reactive trace gases observed in Venus' atmosphere are also present in Earth's atmosphere, but at much lower abundances. The sources and sinks of these reactive trace gases are also generally different on Venus and Earth. For example, SO₂ has an abundance <1 ppmv in the terrestrial troposphere and is mainly due to anthropogenic emissions and to a lesser extent volcanic outgassing. Carbonyl sulfide is present at about 0.5 ppbv in Earth's troposphere (versus ~4400 ppbv on Venus) and is mainly due to biogenic emissions (instead of volcanic outgassing and sulfide chemical weathering on

Venus). Most of the sulfur at the surface of the Earth is in sedimentary deposits of gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (28%) and pyrite FeS_2 (57%), or as sulfate dissolved in the oceans (15%). Hydrogen chloride (~ 1 ppbv) and HF (~ 0.03 ppbv) are virtually absent from Earth's troposphere. Methyl chloride (CH_3Cl) present at ~ 0.5 ppbv and the chlorofluorocarbon (CFC) gases are the major Cl and F gases. The two major CFC gases are CF_2Cl_2 (~ 0.4 ppbv) and CFCl_3 (~ 0.2 ppbv). Methyl chloride results from biogenic emissions but the CFC gases are produced industrially and have no natural sources. The atmospheric inventories of F and Cl are negligible in comparison to the oceanic and crustal inventories. About 75% of all Cl at Earth's surface is Cl^- dissolved in the oceans and essentially all F is found in the crust (Lodders and Fegley, 1997). However, the crustal (or oceanic) inventories of S, Cl, and F on Earth are much larger than the atmospheric inventories of these elements on Venus. This suggests that significant amounts of S, Cl, and F are in Venus' lithosphere instead of being completely degassed into its atmosphere.

The Earth's atmosphere contains over 10,000 times more O_2 than Venus' atmosphere and $\sim 15,000$ times more O_2 than the Martian atmosphere. Photosynthesis is the major source of O_2 in the terrestrial atmosphere and accounts for the large disparities between O_2 on Earth or on Venus and Mars.

The major differences between Venus' atmosphere and the terrestrial atmosphere are as follows. (1) Venus' atmosphere contains large amounts of C, S, Cl, and F relative to the atmospheric inventories on Earth. The high temperatures on Venus outgas these rock-forming elements into its atmosphere. (2) The large amounts of CO_2 and SO_2 driven into Venus' atmosphere maintain a super-greenhouse effect and a surface temperature over three times higher than the blackbody temperature. (3) Venus' atmosphere is much drier than Earth's atmosphere. However the tiny amount of atmospheric water vapor on Venus also helps to maintain the super-greenhouse. (4) Venus' atmosphere contains only trace amounts of O_2 , which is the second most abundant gas on Earth because of the presence of life. As mentioned earlier, Venus' lack of water is primarily responsible for all these differences.

Origin of Venus' Volatile Inventory

The Sun and all the planets in our solar system formed about 4.56 billion years ago from a cloud of gas and dust known as the solar nebula. The elemental abundances in the solar nebula were the same as those in the Sun when it formed and are known as solar system abundances (Lodders 2003). Figure V1 shows a

comparison of the abundances of chemically reactive volatile elements (e.g., H, C, N, S, Cl, F) and chemically inert volatile elements (Ne, Ar, Kr, Xe) on Venus and Earth relative to their solar system abundances. The volatile elements H, C, and N are plotted as H₂O, CO₂, and N₂ in Figure V1 because these are the major gases of these elements in the atmospheres of Venus and Earth. The volatiles plotted in the figure are depleted relative to their solar system abundances because Venus and Earth captured only part of the solar system abundance of each volatile during their formation. However, the chemically reactive volatiles are not as depleted as the noble gases. For example, Venus contains about 10⁻⁹ of the Ne solar system abundance but has about 10⁻⁵ of the N solar system abundance. Nitrogen and neon have similar atomic weights (14.007 vs. 20.183) and have similar solar system abundances (1.95 × 10⁶ atoms vs. 2.15 × 10⁶ atoms). However, nitrogen forms minerals such as osbornite (TiN), sinoite (Si₂N₂O), and carlsbergite (CrN), while neon is inert and does not. Likewise Earth contains about 2 × 10⁻⁹ of the argon solar system abundance and about 7 × 10⁻⁵ of the sulfur solar system abundance. Sulfur and argon also have similar atomic weights (32.06 vs. 36.32 for primordial argon) and similar solar system abundances (4.45 × 10⁵ atoms vs. 1.02 × 10⁵ atoms). Sulfur occurs in troilite (FeS) and other minerals, but argon does not form minerals. The larger depletions of noble gases and the smaller depletions of chemically reactive volatiles suggest that the atmospheres of Earth (e.g., Brown 1949) and Venus primarily formed from volatile-bearing solids that outgassed during and after planetary accretion. The occurrence of volatile-bearing minerals in chondritic meteorites, which are relatively unaltered samples of nebular material, supports this argument.

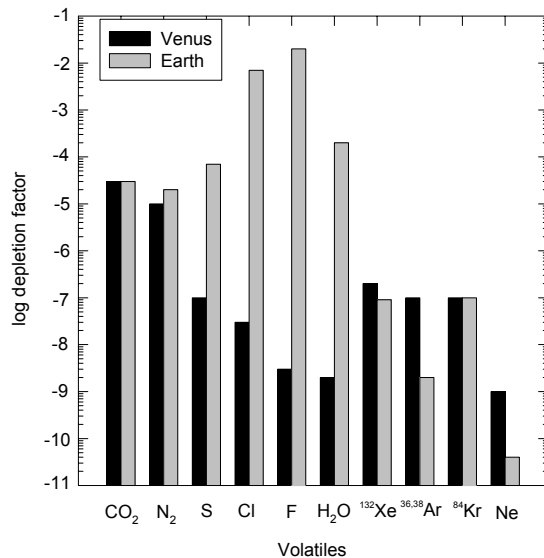


Figure V1. Depletions of chemically reactive volatiles and noble gases on Venus and Earth relative to their solar system abundances.

Two observations suggest that Venus and Earth may have captured some nebular gas during their formation. Recent work on hafnium-tungsten (Hf–W) dating of meteorites indicates rapid accretion and early core formation for the terrestrial planets within the first 30 million years of solar system history (Yin et al. 2002; Kleine et al. 2002). In Cameron’s (1995) model of the solar nebula, the loss of nebular gas, which is the last stage of nebular evolution, takes 3–30 million years. A possible implication of the Hf–W dating is that the terrestrial planets accreted in the presence of residual nebular gas and captured some of it. However, the nebular lifetime is uncertain and the recent Hf–W results are somewhat controversial. The second observation is that ^3He is currently degassing from the Earth’s mantle. This discovery led to a large amount of work on the isotopic composition of other noble gases released from Earth’s mantle. There is some evidence for degassing of Ne with solar isotopic ratios (primordial Ne), but there is little or no evidence for degassing of primordial Ar, Kr, or Xe from Earth’s mantle (Ozima and Podosek 2002). Pepin and Porcelli (2002) discuss the origin of noble gases on Venus, Earth, and Mars in some detail.

Dry vs. Wet Accretion of Venus

Figure V1 graphically shows Venus’ depletion in water relative to the Earth (about a factor of 270,000). As mentioned earlier, Venus may have formed “dry”, or may have formed “wet” and subsequently lost most of its water. An initially “dry” Venus is predicted by the equilibrium condensation model. This model predicts the chemical composition of gas and grains in the solar nebula as a function of temperature and pressure, which vary as a function of radial distance. The equilibrium condensation model predicts that Venus formed “dry” and that Earth formed “wet” because hydrous minerals were unstable where Venus formed, but stable where Earth formed. Venus’ meager water inventory is the result of cometary impacts over time (Lewis 1974). The equilibrium condensation model explains the density difference between Venus and Earth, first order trends in planetary bulk compositions, and many chemical and mineralogical features of chondritic meteorites (Lewis and Prinn 1984; Kerridge and Matthews 1988).

However, persuasive arguments can be made against an initially “dry” Venus. Dynamical models of planetary accretion predict significant overlap of accretion zones for Venus and Earth (Weidenschilling 1976). The overlap would lead to similar water inventories on the two planets. A second argument is that hydrous mineral formation is probably impossibly slow at the cooler temperatures where hydrous minerals

are thermodynamically stable in the solar nebula (Fegley 2000). This would lead to both planets accreting “dry” rock with water being supplied by subsequent impacts of icy planetesimals and comets that are gravitationally scattered into the inner solar system by the outer planets.

We now consider the alternative that Venus formed “wet” and subsequently lost most of its water. Chondritic meteorites are often used as analogs for the types of material accreted by the terrestrial planets during their formation. Water contents of chondritic meteorites range from 9.5–10.8% (by mass) in the volatile-rich CM and CI carbonaceous chondrites, to 0.3–1.1% in the ordinary (H, L, LL) chondrites (Tables 16.10 and 16.11 of Lodders and Fegley 1998). For comparison, Earth’s hydrosphere corresponds to a water content of about 0.03%. As discussed elsewhere (Lodders and Fegley 1997), Venus, Earth, and Mars each apparently formed from a mixture of chondritic material. In this case, formation of either an initially “moist” or “wet” Venus seems unavoidable. For example, the four component meteorite model of Morgan and Anders (1980) predicts 0.03% water in Venus, which is comparable to Earth’s inventory.

The deuterium (D) to hydrogen (H) atomic ratio in Venusian water is 0.025 ± 0.005 which is about 160 ± 32 times larger than the terrestrial D/H ratio of 1.558×10^{-4} in standard mean ocean water (SMOW). The high D/H ratio strongly suggests Venus originally had more H₂O (equivalent to 4–530 meters of liquid water) and lost most of it over time (Donahue et al. 1997). This interpretation assumes that Venusian water started with a D/H ratio like that of terrestrial ocean water. However, some chondritic meteorites, comets, and interplanetary dust particles have D/H ratios ranging up to 50 times the terrestrial value (cf. Table III of Irvine et al. 2000). It is possible that Venus formed with a higher D/H ratio than the Earth. If so, Venus may have had less water than if it formed with an Earth-like D/H ratio.

Even though the high D/H ratio is a good indicator, it is only indirect proof that Venus was initially “wet”. However, if Venus once had water, hydrous minerals, such as amphiboles, should have formed. Amphiboles are common on Earth and are found in metamorphic and igneous rocks. Experimental studies show that tremolite, one of the most common amphiboles, decomposes very slowly at Venus surface temperatures. Extrapolation of laboratory data shows that 50% decomposition of μm -size grains takes 2.7 billion years, and complete decomposition about 10 times longer. These data indicate tremolite and other amphiboles that formed on Venus during a wetter era in the past could still exist on Venus today and provide evidence that Venus was wet (Johnson and Fegley 2003).

Venus' Accretionary Atmosphere

The terrestrial planets probably formed by the accretion of smaller planetesimals (Wetherill 1980). Impact devolatilization of sufficiently large planetesimals probably generated accretionary atmospheres containing N₂, CO₂, H₂O, and other volatiles once Venus (or Earth) reached about 10% of their present mass (Ahrens 1993). Such accretionary atmospheres are called “steam” atmospheres although H₂O is not necessarily the most abundant gas. Significant amount of H₂, generated by the water gas reaction



or by the oxidation of Fe metal



to FeO-bearing minerals, may have been present in the “steam” atmospheres. Carbon, nitrogen, and sulfur gases such as CO₂, CO, CH₄; N₂, NH₃; and SO₂, H₂S, OCS were probably also present in the “steam” atmospheres with relative abundances dependent upon temperature, pressure, and oxidation state at a given time during planetary formation.

Matsui and Abe (1986) modeled the formation and properties of “steam” atmospheres on Venus and Earth. They found that accretion of planetesimals containing ~0.1% water, similar to that in some ordinary chondrites, led to development of a massive “steam” atmosphere on Venus. The greenhouse effect of this atmosphere trapped so much heat that Venus melted (at ~1500 K) once it reached about 40% of its current radius. The mass of Venus’ “steam” atmosphere reached about 10²¹ kg (P ~100 bar), comparable to that of Earth’s present hydrosphere, and was controlled by solubility of water in molten silicate magma. However, Matsui and Abe’s (1986) conclusions are somewhat model dependent, and the existence and fate of a “steam” atmosphere on Venus remain unclear (Pollack 1991).

After Venus had formed, its “steam” atmosphere may have rained out to form hot oceans or all the water may have remained in the atmosphere if the surface temperature remained above the critical point of water (647 K). Some of the water dissolved in the silicate magma may have crystallized as kaersutite, hornblende, or other igneous amphiboles. But, whether or not Venus ever had a “steam” atmosphere, the evolution of Venus’ water inventory is closely connected to the origin of the runaway greenhouse.

Origin of the Runaway Greenhouse and Water Loss

Models by Ingersoll (1969) and Rasool and deBergh (1970) qualitatively showed that Venus has a runaway greenhouse effect while Earth does not because Venus formed closer to the Sun. Once some H₂O or CO₂ was in Venus' atmosphere, greenhouse warming led to sufficiently high surface temperatures to vaporize water and thermally decompose carbonates. Rasool and deBergh (1970) also suggest that reaction (1) and its analogs may have regulated the increasing CO₂ pressure as a function of temperature.

In both models UV sunlight decomposed H₂O to its constituent elements with hydrogen loss to space. The hydrogen loss rates on Venus and Earth today (and presumably in the past) are controlled by the total H atom mixing ratio ($f_{\Sigma H}$) at the homopause (above which diffusive separation of gases occurs)

$$f_{\Sigma H} = f_H + 2f_{H_2} + 2f_{H_2O} + f_{HCl} + f_{HF}. \quad (5)$$

Venus' hydrogen loss rate is currently $\sim 10^7$ H cm⁻²s⁻¹, which could remove a global water layer only 21 cm thick over the age of the solar system. Loss rates $\sim 10^5$ times larger are required to remove an ocean's worth of water in a geologically short time. These occur during hydrodynamic escape, which could have been driven by the significantly higher extreme UV flux that is expected from the early Sun. A hydrodynamic flux of $\sim 10^{12}$ H cm⁻²s⁻¹ could remove ~ 470 meters of water from Venus in 100 million years and produce the elevated D/H ratio observed on Venus today (e.g., Donahue et al. 1997).

However, astrophysical models predict that the early Sun's visible solar flux was about 25–30% less than today. Because of the lower solar flux the runaway greenhouse (and water loss) may have happened some time after Venus formed, rather than right away (Pollack 1991). Hydrodynamic escape of hydrogen is not viable once the solar extreme UV flux has declined. Instead, hydrogen loss occurs ~ 100 times slower via other non-thermal processes that remove much less water from Venus over time (~ 47 meters per 10^9 years). An initially "moist" Venus may be more likely than an initially "wet" Venus.

Huge amounts of residual O₂ are left after losing an ocean's worth of hydrogen. For example, the loss of 2.7 km of water from Venus, equivalent to Earth's oceans, would leave behind 1.1×10^{21} kg of O₂, about 35 times the total amount of O₂ produced by photosynthesis on Earth over time. Loss of 470 meters of water leaves behind 1.9×10^{20} kg of O₂, about six times Earth's total photosynthetic oxygen. The disposal of so much oxygen is a formidable problem. One possibility is oxygen loss to space. This occurs

on Venus today at a rate that would leave behind ~30% of the oxygen in water. But if oxygen was not lost to space, all of it had to be consumed by chemical reactions.

On Earth about 96% of all O₂ produced over time was consumed by oxidation of reduced carbon, iron, and sulfur compounds and only 4% resides in the atmosphere. Currently, the major O₂ sinks on Earth are oxidation of organic carbon to CO₂ (1.6×10^{11} kg yr⁻¹), ferrous to ferric iron (4.7×10^{10} kg yr⁻¹), and sulfides to sulfate (6.2×10^{10} kg yr⁻¹), summing to 2.69×10^{11} kg O₂ yr⁻¹ (Warneck 1988). Oxidation of reduced carbon accreted by Venus plausibly happened during impact devolatilization. This leaves oxidation of reduced iron and sulfur in Venus' lithosphere as possible O₂ sinks. The XRF elemental analyses of Venus' surface found iron (8-9% "FeO") and sulfur (0.9-4.7% SO₃), whose abundances are conventionally reported as oxides although their chemical form is unknown. The sulfur content of Venus' lithosphere is probably closer to that in Earth's mantle (0.04%) or oceanic crust (0.1%) than that found on the surface because reaction (2) adds sulfur by chemical weathering. If Venus' lithosphere initially contained 10% "FeO", which is oxidized to hematite (Fe₂O₃) or magnetite (Fe₃O₄), 1.9×10^{20} kg of O₂ would have to react with 0.5-0.8% of the lithosphere to be consumed. Removal of all this O₂ over 100 million years while water is lost requires a volcanic eruption rate of ~ 140 km³ yr⁻¹ to expose this much lithosphere to the atmosphere. For comparison Earth's volcanism rate is ~ 20 km³ yr⁻¹, and the estimated rate on Venus is 1 km³ yr⁻¹ (see below). A 100 million year removal rate also corresponds to a sink of $\sim 1.9 \times 10^{12}$ kg O₂ yr⁻¹, which is ~ 7 times larger than the current O₂ loss rate on Earth. It is difficult to see how so much O₂ could be lost so rapidly on Venus or how so much lithosphere could be exposed so rapidly. It again seems that an initially "moist" Venus is more plausible than an initially "wet" Venus.

Volcanic Outgassing and Climate Change

As mentioned earlier, CO₂, SO₂, and H₂O are the three most important greenhouse gases in Venus' atmosphere. All three gases are common constituents of terrestrial volcanic gases and volcanism is a probable source for all three gases on Venus. Furthermore, all three gases are probably involved in atmosphere-lithosphere reactions on Venus. These and other arguments suggest that atmospheric chemistry and physics, climate, and volcanism are closely linked on Venus (e.g., Bullock and Grinspoon 2001).

The relative abundances of SO₂, OCS, H₂S, and elemental sulfur vapor (dominantly S₂) in Venusian volcanic gases are unknown. Sulfur dioxide is generally the major sulfur compound in basaltic volcanic gases on Earth, followed by H₂S, OCS, and elemental sulfur vapor. Venusian basalts probably erupt at higher or similar temperatures as terrestrial basalts. If Venusian volcanic gases are as oxidized as (or more oxidized than) terrestrial volcanic gases, SO₂ should be the major sulfur gas. More oxidized gases may also contain up to ~200 ppmv SO₃, which may provide an observational test for water loss and O₂ consumption on Venus. The large CO₂ and very low H₂O abundances in Venus' atmosphere imply that S₂ and OCS should be more abundant than H₂S in Venusian volcanic gases. For comparison, SO₂ and S₂ are the two major species in volcanic gases on Io which has apparently lost all or most hydrogen and carbon.

As discussed earlier, reaction (2) would remove all SO₂ (and thus the sulfuric acid clouds) from Venus' atmosphere in ~1.9 million years in the absence of a volcanic source. Sulfur dioxide undergoes similar reactions with other calcium-bearing minerals such as anorthite, diopside, and wollastonite. The measured Ca/S ratios are greater than unity at the *Venera 13*, *14*, and *Vega 2* sites. These ratios are larger than one, which is the expected value if all Ca were combined with S in anhydrite. Thus loss of atmospheric SO₂ via chemical weathering of Ca-bearing minerals on Venus' surface is probably an ongoing process.

Maintenance of atmospheric SO₂ at current levels requires eruption of ~1 km³ yr⁻¹ of lava with the average composition of the *Venera 13*, *14*, and *Vega 2* landing sites. This volcanism rate is the same as the average rate of subaerial volcanism on Earth and is about 5% of the total volcanism rate of ~20 km³ yr⁻¹. The required sulfur eruption rate to maintain SO₂ on Venus at steady state is ~2.8 × 10¹⁰ kg yr⁻¹. This is similar to the SO₂ emission rates of 9 × 10⁹ kg yr⁻¹ (subaerial), 1.9 × 10¹⁰ kg yr⁻¹ (submarine), and 2.8 × 10¹⁰ kg yr⁻¹ (total) from terrestrial volcanism (Charlson et al. 1992).

Volcanism on Earth and on Io are episodic. By analogy Venusian volcanism should be episodic, which may be one reason why active volcanism has not yet been seen on Venus. However a volcanic source for SO₂ is required at present. What may happen if the volcanic source and anhydrite sink for SO₂ are not balanced? If less SO₂ is erupted than is lost by anhydrite formation, less SO₂ will be left in the atmosphere, less H₂SO₄ will be produced, and fewer clouds will form. Temperatures in Venus' atmosphere and at the surface may decrease because SO₂ and volcanic volatiles such as CO₂ and H₂O are greenhouse gases. The carbonates magnesite (MgCO₃) and dolomite (CaMg(CO₃)₂) may become stable and consume atmospheric

CO₂ as temperatures drop. Conversely if more SO₂ is erupted than is lost by anhydrite formation, more SO₂ will be added to the atmosphere, more H₂SO₄ will be produced, and more clouds will form. In this case atmospheric and surface temperatures may rise as more greenhouse gases enter the atmosphere. Minerals now stable at 740 K on Venus' surface may decompose as temperatures increase, releasing more volatiles into the atmosphere (e.g., HCl, HF, elemental sulfur vapor). Some of these effects, which could operate in the future and may have done so in the past, have been studied in climate models that incorporate variations of SO₂ and H₂O abundances on the clouds and temperatures on Venus (e.g., Bullock and Grinspoon 2001). In particular, large temperature changes are predicted to result from the putative global resurfacing of Venus 500±200 million years ago.

Acknowledgements. I thank V. Gornitz for her patience, K. Lodders for comments, and L. Schaefer for her assistance with manuscript preparation. This work was supported by Grants NAG5-11037 and NAG5-11050 from the NASA Planetary Atmospheres Program.

Bruce Fegley, Jr.

Bibliography

- Ahrens, T. J., 1993. Impact erosion of terrestrial planetary atmospheres. *Annu. Rev. Earth Planet. Sci.* **21**, 525-555.
- Barsukov V. L., Basilevsky, A. T., Volkov, V. P., and Zharkov, V. N. (eds.) 1992. *Venus Geology, Geochemistry, and Geophysics*. Tucson, AZ: Univ. of Arizona Press, 421 pp.
- Bézard, B., DeBergh, C., Fegley, B., Maillard, J. P., Crisp, D., Owen, T., Pollack, J. B., and Grinspoon, D., 1993. The abundance of sulfur dioxide below the clouds of Venus. *Geophys. Res. Lett.* **20**, 1587-1590.
- Bougher S. W., Hunten, D. M., and Phillips, R. J. (eds.), 1997. *Venus II*. Tucson, AZ: Univ. of Arizona Press, 1362 pp.
- Brown, H., 1949. Rare gases and the formation of the Earth's atmosphere. In Kuiper, G. P. (ed.), *The Atmospheres of the Earth and Planets*. Chicago, IL: Univ. of Chicago Press, pp. 260-268.
- Bullock, M.A. and Grinspoon, D.H., 2001. The recent evolution of climate on Venus. *Icarus* **150**, 19-37.
- Cameron, A. G. W., 1995. The first ten million years in the solar nebula. *Meteoritics* **30**, 133-161.
- Chamberlain, J. W. and Hunten, D. M., 1987. *Theory of Planetary Atmospheres*. San Diego, CA: Academic Press, 481 pp.
- Charlson R. J., Anderson T. L., and McDuff R. E. 1992. The sulfur cycle. In *Global Biogeochemical Cycles* (eds. S. S. Butcher, R. J. Charlson, G. H. Orians, and G. V. Wolfe), pp. 285-300. Academic Press.

- Donahue, T. M., Grinspoon, D. H., Hartle, R. E., and Hodges, R. R., Jr., Ion/neutral escape of hydrogen and deuterium: Evolution of water. In Bougher S. W., Hunten, D. M., and Phillips, R. J. (eds), *Venus II*, Tucson, AZ: Univ. of Arizona Press, pp. 385-414.
- Fegley, B. Jr., 2000. Kinetics of gas-grain reactions in the solar nebula. *Space Sci. Rev.* **92**, 177-200.
- Fegley, B. Jr., Venus, 2004. In Davis, A. M. (ed), *Meteorites, Comets, and Planets*. Holland, H. D. and K. K. Turekian, (eds), *Treatise on Geochemistry*, Vol. 1, Oxford, England: Elsevier-Pergamon, pp. 487-507.
- Hunten, D. M., Colin, L., Donahue, T. M., and Moroz, V. I. (eds), 1983. *Venus*. Tucson, AZ: Univ. of Arizona Press, 1143 pp.
- Ingersoll, A.P., 1969. The runaway greenhouse: A history of water on Venus. *J. Atmos. Sci.*, **26**, 1191-1198.
- Irvine, W. M., Schloerb, F. P., Crovisier, J., Fegley, B., Jr., and Mumma, M. J., Comets: A link between interstellar and nebular chemistry, 2000. In Mannings, V., Boss, A. P., and Russell, S. S. (eds), *Protostars and Planets IV*. Tucson, AZ: Univ. of Arizona Press, pp. 1159-1200.
- Johnson, N.M. and Fegley, B. Jr., 2003. Tremolite decomposition on Venus II. Products, kinetics, mechanism. *Icarus*, **164**, 317-333.
- Kargel, J. S., Komatsu, G., Baker, V. R., and Strom, R. G., 1993. The volcanology of Venera and VEGA landing sites and the geochemistry of Venus. *Icarus*, **103**, 253-275.
- Kargel, J. S., Kirk, R. L., Fegley, B., Jr. and Treiman, A., 1994. Carbonate-sulfate volcanism on Venus? *Icarus* **112**, 219-252.
- Kaula, W. M., 1999. Constraints on Venus evolution from radiogenic argon. *Icarus*, **139**, 32-39.
- Kerridge, J. and Matthews, M. S. (eds), 1988. *Meteorites and the Early Solar System*. Tucson, AZ: Univ. of Arizona Press, 1269 pp.
- Kleine, T., Münker, C., Mezger, K., and Palme, H., 2002. Rapid accretion and early core formation on asteroids and terrestrial planets from Hf-W chronometry. *Nature* **418**, 952-955.
- Krasnopolsky, V. A., 1986. *Photochemistry of the Atmospheres of Mars and Venus*. Berlin, Germany: Springer-Verlag, 334 pp.
- Lewis, J. S., 1974. Volatile element influx on Venus from cometary impacts. *Earth Planet. Sci. Lett.* **22**, 239-244.
- Lewis, J.S. and Prinn, R.G., 1984. *Planets and Their Atmospheres: Origin and Evolution*. New York, NY: Academic Press, 470 pp.
- Lodders, K., 2003. Solar system abundances and condensation temperatures of the elements. *Astrophys. J.* **591**, 1220-1247.
- Lodders, K. and Fegley, B., Jr., 1997. An oxygen isotope model for the composition of Mars. *Icarus* **126**, 373-394.
- Lodders, K. and Fegley, B., Jr., 1998. *The Planetary Scientist's Companion*. New York, NY: Oxford University Press, 371 pp.
- Matsui, T. and Abe, Y., 1986. Impact-induced atmospheres and oceans on Earth and Venus. *Nature*, **322**, 526-528.
- Morgan, J. W. and Anders, E., 1980. Chemical composition of the Earth, Venus, and Mercury. *Proc. Natl. Acad. Sci.* **77**, 6973-6977.
- Ozima, M. and Podosek, F. A., 2002. *Noble Gas Geochemistry*. 2nd ed. Cambridge, England: Cambridge University Press, 286 pp.
- Pepin, R. O. and Porcelli, D., 2002. Origin of noble gases in the terrestrial planets. In Porcelli, D., Ballentine, C. J., and Wieler, R. (eds), *Noble Gases in Geochemistry and Cosmochemistry*, Reviews in Mineralogy and Geochemistry Vol. 47, Washington, D.C.: Mineralogical Society of America, pp. 191-246.
- Pollack, J. B., 1991. Kuiper Prize Lecture: Present and past climates of the terrestrial planets. *Icarus*, **91**, 173-198.
- Prinn, R.G. and Fegley, B. Jr., 1987. The atmospheres of Venus, Earth, and Mars: A critical comparison. *Annual Rev. Earth Planet. Sci.* **15**, 171-212.
- Rasool, S. I. and DeBergh, C., 1970. The runaway greenhouse and the accumulation of CO₂ in the Venus atmosphere. *Nature* **226**, 1037-1039.

- Shirley, J.H. and Fairbridge, R.W. (eds.) 1997 *Encyclopedia of Planetary Sciences*. London, England: Chapman & Hall, 990 pp.
- Symonds R. B., Rose W. I., Bouth G. J. S., and Gerlach T. M. 1994. Volcanic-gas studies: Methods, results, and applications. In *Volatiles in Magmas* (eds. M. R. Carroll and J. R. Holloway), pp. 1-66. Mineralogical Society of America.
- Warneck, P., 1988. *Chemistry of the Natural Atmosphere*. San Diego, CA: Academic Press, 757 pp.
- Weidenschilling, S. J., 1976. Accretion of the terrestrial planets II. *Icarus* **27**, 161-170.
- Wetherill, G. W., 1980. Formation of the terrestrial planets. *Annu. Rev. Astron. Astrophys.* **18**, 77-113.
- Yin, Q., Jacobsen, S. B., Yamashita, K., Blichert-Toft, J., Télouk, P., and Albarède, F., 2002. A short timescale for terrestrial planet formation from Hf-W chronometry of meteorites. *Nature* **418**, 949-952.
- Yung, Y.L. and DeMore, W.B., 1999. *Photochemistry of Planetary Atmospheres*. New York, NY: Oxford University Press, 456 pp.

Cross-references

Atmospheric evolution, Earth

Atmospheric evolution, Mars

Carbon cycle

“Greenhouse” (warm) climates

Volcanic eruptions and climate change

Weathering and climate

Table VI. Some properties of Venus and Earth (after Lodders and Fegley, 1998)

Property	Venus	Earth
Semi-major axis (10^6 km)	108.21	149.60
(A.U.)	0.7233	1.00
Average radius (km)	6051.4	6371.0
Mass (10^{24} kg)	4.8685	5.9736
Density (kg m^{-3})	5,243	5,515
Volume (10^{10} km ³)	92.84	108.3
Lithospheric mass (10^{24} kg)	3.14 (64.5%)	4.03 (67.5%)
Core mass (10^{24} kg)	1.73 (35.5%)	1.94 (32.5%)
Lithospheric volume (10^{10} km ³)	78.2 (84.2%)	90.6 (83.7%)
Core volume (10^{10} km ³)	14.6 (15.8%)	17.7 (16.3%)
Escape velocity (km s^{-1})	10.361	11.186
Sidereal orbital period (days)	224.70	365.26
Average length of day	116.75	1.0
Mean gravitational acceleration (m s^{-2})	8.870	9.820
Solar constant (W m^{-2})	2613.9	1367.6
Geometric albedo	0.76	0.30
Absorbed solar energy (W m^{-2})	627.3	957.3
Mean surface temperature (K)	740	288
Black body temperature (K)	240	250
Mean surface pressure (bar)	95.6	1.0
Scale height at surface (km)	15.90	8.42
Atmospheric lapse rate at surface (K km^{-1})	8.0	6.5
Dry adiabatic lapse rate at surface (K km^{-1})	7.8	9.8
Atmospheric composition of dry gas	CO ₂ (96.5%), N ₂ (3.5%), SO ₂ (0.015%)	N ₂ (78.1%), O ₂ (20.9%), Ar (0.93%), CO ₂ (0.036%)
Atmospheric mean formula weight (g mol^{-1})	43.45	28.97
Atmospheric mass (10^{18} kg)	495	5.28
Atmospheric water vapor ^a	0.003%	1 – 4%
Cloud composition and coverage (%)	H ₂ SO ₄ (100%)	H ₂ O (50%)
Important greenhouse gases	CO ₂ , SO ₂ , H ₂ O	CO ₂ , H ₂ O, CH ₄ , N ₂ O, CFCs ^b

^aTropospheric values. Water vapor is only a few ppmv in Earth's stratosphere and above Venus' clouds.

^bCFC gases are chlorofluorocarbon gases such as CF₂Cl₂, CFCl₃, and CF₄

Table V2. Chemical composition of Venus' atmosphere^a

Gas	Abundance	Source(s)	Sink(s)	Comments
CO ₂	96.5±0.8%	Outgassing	Solar UV photolysis, carbonate formation	Major greenhouse gas 2.7, 4.3, 15 μm bands
N ₂	3.5±0.8%	Outgassing	NO _x formation by lightning	Altitude-dependent mixing ratio needs confirmation
SO ₂ ^b	0.01-1 ppmv (cloud top) 150±30 ppmv (22–42 km) 25–150 ppmv (12–22 km)	Outgassing, and oxidation of OCS and H ₂ S	Photochemical oxidation to H ₂ SO ₄ cloud droplets, reaction with Ca-bearing minerals on Venus' surface to form anhydrite (CaSO ₄), reduction to OCS & H ₂ S	Most abundant sulfur gas, important greenhouse gas 7.3, 8.7, 19.3 μm bands
H ₂ O ^b	30±15 ppmv (0–45 km)	Outgassing, and cometary impacts	Hydrogen escape to space, and oxidation of ferrous iron minerals	Most abundant hydrogen gas, important greenhouse gas 0.9, 2.7, 6.3 μm bands
⁴⁰ Ar	31 ⁺²⁰ ₋₁₀ ppmv	Outgassing (⁴⁰ K decay)		About 3-4 times less ⁴⁰ Ar than on Earth (g/g basis)
³⁶ Ar	30 ⁺²⁰ ₋₁₀ ppmv	Outgassing (primordial)		About 70 times more ³⁶ Ar than on Earth (g/g basis)
CO ^b	45±10 ppmv (cloud top) 30±18 ppmv (42 km) 28±7 ppmv (36–42 km) 20±3 ppmv (22 km) 17±1 ppmv (12 km)	CO ₂ photolysis, and outgassing	Photochemical oxidation to CO ₂ via catalytic cycles. Also consumed by thermochemical reactions with sulfur gases and ferric iron minerals.	4.66 μm fundamental, potentially important greenhouse gas, involved in Venus atmospheric sulfur cycle
⁴ He ^c	0.6–12 ppmv	Outgassing (U, Th decay)	Escape to space	
Ne	7±3 ppmv	Outgassing (primordial)		About 20 times more Ne than on Earth (g/g basis)
³⁸ Ar	5.5 ppmv	Outgassing (primordial)		
OCS ^b	4.4±1 ppmv (33 km)	Outgassing, sulfide weathering	Conversion to SO ₂	4.8, 11.6, 19.1 μm bands
H ₂ S ^b	3±2 ppmv (<20 km)	Outgassing, sulfide weathering	Conversion to SO ₂	3.8, 4.2, 8.5 μm bands
HDO ^b	1.3±0.2 ppmv (sub-cloud)	Outgassing	Hydrogen escape to space	
HCl	0.6±0.12 ppmv (cloud top) 0.5 ppmv (35–45 km)	Outgassing	Formation of Cl-bearing minerals	3.46 μm fundamental
⁸⁴ Kr	25 ⁺¹³ ₋₁₈ ppbv	Outgassing (primordial)		
SO ^b	20±10 ppbv (cloud top)	Photochemistry	Photochemistry	
S ₁₋₈ ^b	20 ppbv (<50 km)	Sulfide weathering, outgassing	Conversion to SO ₂	
HF	5 ⁺⁵ _{-2.5} ppbv (cloud top) 4.5 ppbv (35–45 km)	Outgassing	Formation of F-bearing minerals	2.52 μm fundamental
¹³² Xe	<10 ppbv	Outgassing (primordial)		
¹²⁹ Xe	<9.5 ppbv	Outgassing (¹²⁹ I decay)		

Modified from Fegley (2004). ^aAbundance by volume, ppm = parts per million by volume, ppb = parts per billion by volume

^bThe abundances of these gases are altitude-dependent. ^cThe He abundance has only been measured above the homopause where diffusive separation occurs. This value is 12⁺²⁴₋₆ ppm by volume (von Zahn et al., 1983). The value listed above is a model-dependent extrapolation below the homopause.