Atmospheric Chemistry

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A Reverse Ozone Hole on Mars

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heterogeneous chemistry · ice clouds · mars atmosphere · ozone · radical reactions

Until recently, atmospheric chemists have not taken a very active interest in our red, frosty neighboring planet Mars (Figure 1). The thin Martian atmosphere appeared to merely support an arid and dusty environment, being composed of 95 % CO_2, minor amounts of N_2 and Ar, and trace amounts of O_2, CO, and H_2O. An interesting aspect, however, which was resolved long ago, is how the CO_2 atmosphere is preserved photochemically.[1,2] Solar ultraviolet (UV) radiation photodissociates CO_2, while the reverse process is controlled by hydroxyl (OH) radicals produced by the photodissociation of water vapor:

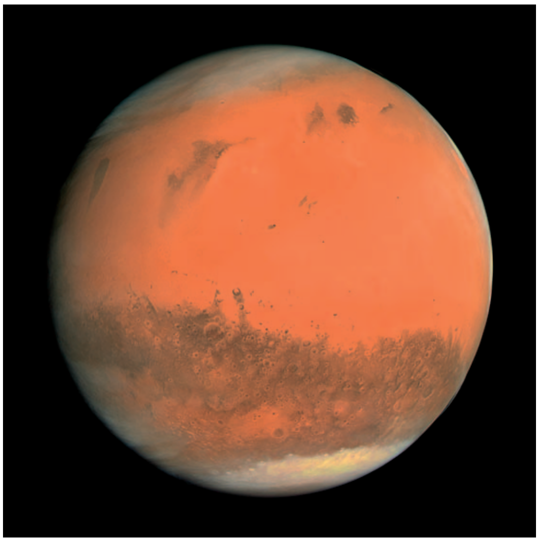

Figure 1. True-color image of Mars, showing the south polar ice cap and thin ice clouds (photo ESA).

$$CO_2 + h\nu \rightarrow CO + O \quad (\lambda < 220\,\text{nm}) \tag{1}$$

$$CO + OH \rightarrow CO_2 + H \tag{2}$$

Subsequently, the OH is recycled by the following processes:

$$H + O_2 + M \rightarrow HO_2 + M \tag{3}$$

$$HO_2 + O \rightarrow O_2 + OH \tag{4}$$

(M is a third body with the concentration of the ambient atmosphere). Contrary to the situation on Earth, the UV radiation penetrates deeply into the Martian atmosphere, because the levels of oxygen and ozone are low.[3]

However, this is not the whole story. New satellite data of the Mars atmosphere have provided important information about trace gas distributions, which has revitalized scientific interest. Most emphasis has been on gas-phase reactions, which are included in a chemistry–climate model.[4] Furthermore, much progress has been made in modeling the atmospheric water cycle, including ice clouds.[5] Recent model calculations that also account for heterogeneous chemistry on ice particles suggest that the combination of these processes plays an important role in controlling the stability and composition of the Martian atmosphere.[6] This Highlight contrasts the conditions on Mars and Earth in light of these discoveries and comes across some intriguing features.

By comparing the two planets we notice striking similarities as well as differences. Both have rotational periods (sols) of about 24 h, whereas the seasons on Mars are nearly twice as long as on Earth. The planetary rotations give rise to instabilities in the atmospheric Hadley circulations, which therefore break up into cells (Figure 2). The inclinations of the rotational axes (obliquities) are also very similar, about 24°, whereas the eccentricity of the Mars orbit around the Sun is much larger (0.093) compared to Earth (0.017). In an eccentric orbit (i.e. elliptical rather than circular), the point in time at which the planet is closest to the Sun is called perihelion and the largest distance is reached at aphelion.

On Mars, the atmospheric greenhouse effect is weak and the amplitude of the seasonal cycle large, so that winters at aphelion are extremely cold, especially over the south pole. The thin Martian atmosphere has a low heat capacity and hence responds sensitively to variations in solar radiation. On Earth, the mean surface temperature is 288 K, whereas on Mars it is 222 K. In the cold season, part of the Martian CO_2 atmosphere freezes into the polar ice cap ($T \approx 125$ K), which can cause a pressure drop of 25 %.

On Earth as well as Mars the formation of clouds plays an important role in the water cycle and the atmospheric composition. Although our atmosphere is much more humid than that on Mars, the cold and low-density conditions there give rise to a high relative humidity, so that ice clouds are

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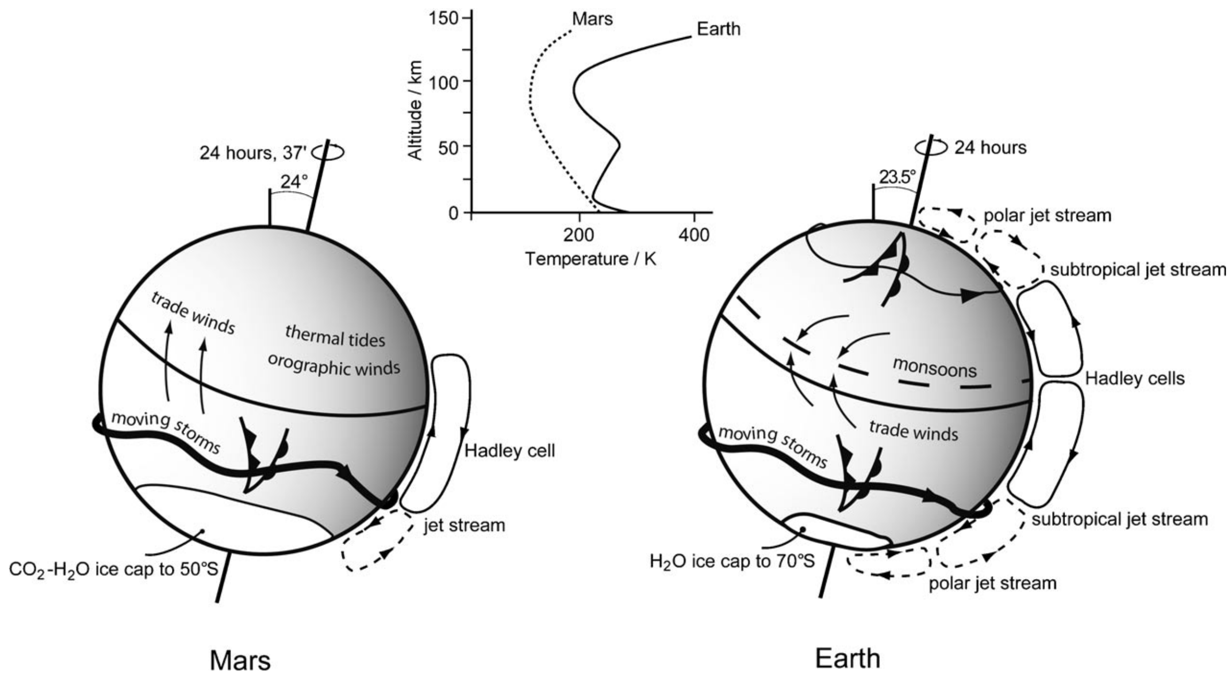

Figure 2. Planetary and atmospheric characteristics during northern summer.

abundant. Martian clouds are particularly frequent over the poles, where they are referred to as polar hoods, and over the high volcanic mountains.[7] The highest mountain is Olympus Mons, about 100 times the size of the largest Earth volcano and nearly three times higher than Mount Everest. On both planets such high mountains are regularly covered in clouds. Furthermore, during Martian aphelion an extensive equatorial cloud belt develops in the upward branch of the Hadley circulation.

On Mars, the radii of the ice-cloud particle are typically a few micrometers. On Earth, they are much larger, up to 100 μm, although in very cold regions, including the lower stratosphere, they can be similarly small. On Earth, polar stratospheric clouds (PSCs) consist of nitric acid trihydrate grown on sulphuric acid aerosols at temperatures below 195 K. In extremely cold conditions in winter, especially over Antarctica, additional water condenses onto the PSCs, and the particles can grow to several tens of micrometers. As detailed below, the PSCs play a central role in generating the ozone hole.

In the lower parts of our atmosphere, liquid water droplets can only freeze homogeneously below about 235 K, whereas at higher temperatures freezing nuclei are needed. In fact, desert dust particles are particularly efficient ice nuclei.[8] Since dust particles are abundant on Mars (Figure 3), it is likely that they similarly act as nuclei on which the water vapor deposits. As the growing particles accumulate water mass, their settling velocity increases, which helps clear the Martian atmosphere from the dust.

On Mars, the mean ozone column density is less than 1 Dobson unit (DU), equivalent to a layer of less than 10 μm O_3 at standard temperature and pressure (STP; 1 DU = 2.69×10^{20} molecules m^{-2} and 0.447 mmol $O_3\,m^{-2}$). In the Earth's stratosphere (ca. 10–50 km altitude), the O_3 column is more than two orders of magnitude thicker, typically about 300 DU (3 mm O_3 at STP), resulting from the photodissociation of O_2. On Mars, O_3 is formed from the photodissociation of both CO_2 and O_2 and subsequent recombination of O atoms with O_2. The recent Mars Express mission by the European Space Agency (ESA) monitors ozone over a wide range of latitudes and longitudes. The measurements indicate strong spatial and seasonal O_3 gradients, with a global maximum during aphelion and a minimum during perihelion.[9] At the equator and middle latitudes, O_3 column densities are usually less than 0.3 DU, whereas near the poles they can reach 3 DU.

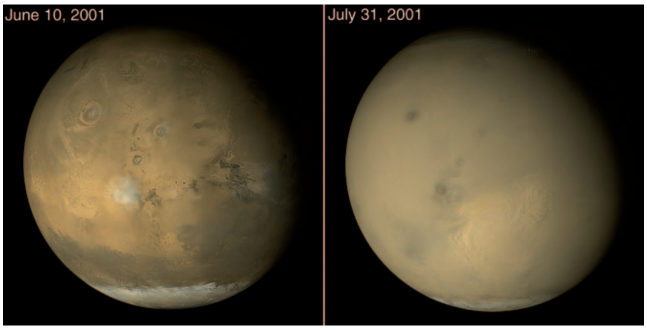

Figure 3. By the end of the Martian winter, widespread dust storms develop that can obscure the entire planet (photos NASA).

On Earth the production of O_3 has a maximum in the equatorial upper stratosphere, whereas the column density is highest over the poles. This "paradox" is explained by meridional transport in the Brewer–Dobson circulation and subsidence over the poles, driven by the equator–pole gradient in solar radiation absorption within the ozone layer and the breaking of waves that propagate from the troposphere. Solar heating also explains the reverse temperature profile between 10 and 50 km altitude (Figure 2). The temperature inversion between the lower atmosphere (troposphere) and stratosphere limits mixing between these layers. This pronounced layering has no equivalent on Mars, where convection determines the mixing height of water vapor up to the hygropause.

It has long been recognized that anthropogenic emissions of nitrogen oxides and halocarbon compounds jeopardize the Earth's ozone layer, whereby the initial focus has been on gas-phase chemistry.[10,11] The O_3 loss is caused by catalytic cycles, for example:

$$X + O_3 \longrightarrow XO + O_2 \quad (5)$$

$$XO + O \longrightarrow X + O_2 \quad (6)$$

$$\text{Net:}\ O_3 + O \longrightarrow 2\,O_2 \quad (7)$$

There can be various X/XO pairs, for example, H/OH, OH/HO_2, NO/NO_2, Cl/ClO, and Br/BrO. Moreover, interactions between XO compounds of different chemical families can enhance the efficiency of O_3 loss. Since the O and X atoms are produced by photodissociation reactions, ozone loss in the polar night is slow.

In the absence of PSCs, several of the X and XO species combine into deactivated "reservoirs", such as HNO_3, HCl, and $ClONO_2$, which can be transported to the troposphere by Brewer–Dobson circulation and then removed by precipitation. However, the cold Antarctic conditions are conducive to the formation of PSCs, which heterogeneously release active chlorine from the reservoir species and remove nitrogen oxides, for example by:[12]

$$ClONO_2(g) + HCl(s) \rightarrow HNO_3(s) + Cl_2(g) \quad (8)$$

In winter the gaseous Cl_2 accumulates in the lower stratosphere. During polar sunrise in early spring, Cl_2 rapidly photodissociates, which causes dramatic ozone loss over the Antarctic continent (Figure 4).

Many of the reactions studied in stratospheric ozone chemistry are applied in photochemical models of the Mars atmosphere (except chlorine chemistry, which can be neglected). Again, the initial focus has been on the gas-phase chemistry. In fact, good agreement between modeled and observed CO concentrations has been interpreted as an indication that there is no need to invoke heterogeneous processes,[13] although this has been a subject of debate.

Water vapor is the prime source of HO_x radicals ($H + OH + HO_2$), and its concentration is negatively correlated to that of ozone owing to reactions such as:

$$H + O_3 \rightarrow OH + O_2 \quad (9)$$

$$O + OH \rightarrow O_2 + H \quad (10)$$

$$OH + O_3 \rightarrow HO_2 + O_2 \quad (11)$$

$$O + HO_2 \rightarrow O_2 + H \quad (12)$$

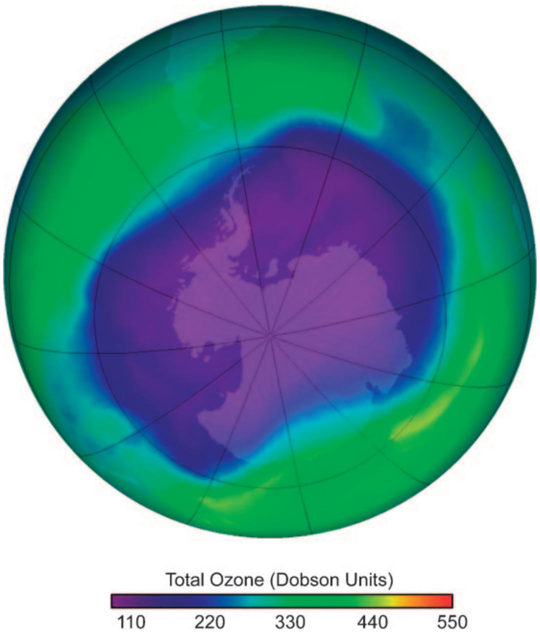

Figure 4. Record loss of approximately 40 million tons of ozone was measured over Antarctica during austral spring in 2006 (NASA/Ozone Monitoring Instrument).

Model results are very sensitive to H_2O concentrations. Previously, water vapor profiles were prescribed, while more recently they have been explicitly simulated by chemistry–climate models,[4,5] even though there is still a need to adjust cloud parameters to improve agreement with observations.[6] A weakness of models is that reaction coefficients, as measured for Earth conditions, may not apply to Mars.[6,14] In the early years of stratospheric ozone research, the poorly characterized kinetics and the speculative extrapolations to atmospheric conditions hampered progress. Clearly, laboratory studies of the conditions on Mars at temperatures of 100–200 K are needed.

The new measurements of the Martian atmosphere by satellites and powerful telescopes show that at high latitudes the O_3 variability can be large.[9] Intriguingly, two ozone layers have been discovered, one near the surface over the poles and one between 30 and 60 km altitude, a dry region above the hygropause.[15] The upper layer only appears at night when HO_x radicals are absent and O atoms recombine with molecular oxygen. It has a maximum depth during aphelion and a minimum during perihelion, when the moist region reaches up to high altitudes. The lower O_3 layer is sensitive to the water vapor abundance near the surface. The data also demonstrate that the negative correlation between H_2O and O_3 is particularly conspicuous over the poles.

While chemistry–climate models of Mars that only include gas-phase chemistry do simulate a seasonal O_3 cycle over the poles, the large amplitude can only be reproduced by invoking heterogeneous chemistry on ice clouds.[6] Several effects are superimposed. During the summer, water vapor is released from the retreating seasonal ice caps,[9] and the photochemistry efficiently produces O_3-destroying HO_x radicals. Conversely, during winter and spring the very low temperatures give rise to cloud formation, which additionally reduces the source of radicals by trapping up to 30% of the water column.[7] Furthermore, the ice clouds provide a surface for heterogeneous HO_x loss.[6] These conditions curb the chemical sinks so that the O_3 concentration strongly increases over the poles. This chronology is reversed compared to that on Earth, as on Mars a pronounced O_3 maximum develops during the dry winter and spring, and O_3 is destroyed in summer.

Clearly, the atmospheric chemistry on Mars is very interesting. Moreover, it might hold clues for conditions on Earth at low halogen loading and low stratospheric temperatures, as induced by high CO_2 levels.

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