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Loss of Oxygen from Venus

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Abstract. Ionization of thermal and non-thermal oxygen atoms above the plasmapause on Venus supplies an escape flux for O averaging 6×10^6 atoms $cm^{-2}sec^{-1}$. Hydrogen and oxygen atoms escape with stoichiometry characteristic of water. It is argued that escape of H is controlled by the oxidation state of the atmosphere, regulated by escape of O.

The origin and evolution of H_2O on Venus has drawn the attention of many scientists over the past decade. Views are diverse, ranging from assumptions that Venus had a primordial ocean [*Walker et al.*,1970], to assertions that the planet was desiccated from the beginning [*Lewis*,1970]. The debate has been relatively unconstrained, bounded on the one hand by analogy with the Earth, on the other by inference drawn from models of condensation in the early solar system.

The scope for speculation is now more limited. The abundance of H_2O in the contemporary atmosphere is defined to within a factor of 2, 10^{-4} v/v [*Moroz et al.*,1979; *Young et al.*,1981]; processes regulating escape of H are better understood [*Kumar et al.*,1978; *Hodges and Tinsley*,1981; *Cravens et al.*,1981; *McElroy et al.*,1982]; and there is evidence that Venus is enriched in D relative to H, [D]/[H] approximately 10^{-2} [*McElroy et al.*,1982; *Donahue et al.*,1982], as compared to 1.6×10^{-4} for Earth.

We argued elsewhere [*McElroy et al.*,1982] that escape of H was driven by momentum transfer from fast O atoms, formed by recombination of O_2^+,

$$O_2 + e \rightarrow O(^3P) + O(^1D) \qquad (1)$$

The O atoms in (1) are formed with speeds of 5.6 km sec^{-1} and approximately 15% of subsequent collisions with thermal H,

$$O^* + H \rightarrow O^* + H^* \qquad (2)$$

lead to production of hot hydrogen atoms, H*, with speeds higher than the velocity for escape, 10.2 km sec^{-1}.

Escape of D by the analogous reaction is trivial and one expects the ratio [D]/[H] to increase with time, by a factor of 10^2 in 4.5×10^9 years. McElroy *et al.*[1982] concluded that the abundance of H_2O on Venus was initially no less than 8×10^2 g cm^{-2}, with escape accounting for loss of at least 5×10^{25} atoms H cm^{-2}.

This paper focuses on loss of O, a topic raised elsewhere by Brace *et al.*[1982] and Luhmann *et al.* [1981]. We argue that the rate for escape of O is presently half that for H, i.e., H and O escape with stoichiometry characteristic of H_2O. A similar situation is thought to apply for Mars [*McElroy and Donahue*, 1972]. We propose that escape of H is regulated by loss of O for both planets at the present epoch. Loss of O on Venus is associated with ionization above the plasmapause; atoms produced in (1) are fast enough to escape directly from Mars [*McElroy*, 1972].

The composition of Venus' exosphere is dominated by O. Ionization of O is followed by

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$$O + CO_2 \rightarrow O_2 + CO \qquad (3)$$

below 200 km, with recombination by (1). Production of O at higher altitudes is balanced by downward diffusive transport. In this case also recombination is through (3) followed by (1) but the net contribution to O* is small. Exospheric O* arises mainly from the region 180 to 200 km and the source ($cm^{-3}sec^{-1}$) may be represented by 2J[O] where J is the ionization frequency (sec^{-1}) and [O] is the density of O (cm^{-3}). The mean intensity of O* ($cm^{-2}sec^{-1}ster^{-1}$) in the source region, defined by analogy to the equivalent concept in radiative transfer [*Chandrasekhar*, 1960], is

$$\bar{I}(O^*) = 2J/(4\pi Q) \qquad (4)$$

where $Q(cm^2)$ is the cross section for momentum transfer between O* and O.

The concentration of O* above 200 km is determined by the flux originating from lower levels. Atoms emanate from the source region with speeds V* of about 5.6 km sec^{-1}. Residence times above 200 km are given by

$$t^* = 2V^*\mu/g \qquad (5)$$

where $\cos^{-1}\mu$ is the angle defined by the initial velocity vector with respect to the vertical and g is the local acceleration of gravity. The column density (cm^{-2}) of primary O* above 200 km is given approximately by

$$N^* = 2\pi\int_0^1 \bar{I}\, t^* \mu d\mu = 2JV^*/(3Qg). \qquad (6)$$

With typical values for J and Q ($J=1.7 \times 10^{-6}$, $Q=1.2 \times 10^{-15}$), N* is $6.4 \times 10^{11} cm^{-2}$.

Collisions between primary O* and O give rise to secondary O*. The net column density of O* is consequently larger than given by (6). The energy distribution ofsecondary O* was treated as follows. We selected m equally spaced intervals, $0 < E_1 < E_2 < ... < E_m$, between 0 and the energy of primaries, $E_m = 2.5$ eV. We assumed that the collision cross section was independent of energy and that scattering was isotropic in the center of mass system. Then, the mean intensity of secondary O* at E_i is given by

$$\bar{I}_i = \left(\frac{2i}{i-1}\right) \cdot \sum_{j=i} \left(\frac{\bar{I}_j}{j}\right) \qquad (7)$$

where

$$\bar{I}_m = \left(\frac{m}{m-1}\right) \cdot \bar{I}(O^*). \qquad (8)$$

The computed energy spectrum for O* is shown in Figure 1. Note that inclusion of secondaries led to an increase by a factor of 4 in the abundance of O* above 0.3eV.

The distribution of O* above 200 km is illustrated in Figure 2. Results were obtained by analyzing ballistic trajectories for atoms entering the the collisionless region with an isotropic distribution of velocities, with an energy spectrum as shown in Figure 1. The mean intensity of primary O* in the source region was specified using (4). We allowed for production of O^+ by photoionization [*Oppenheimer and Downey*,1980] and electron

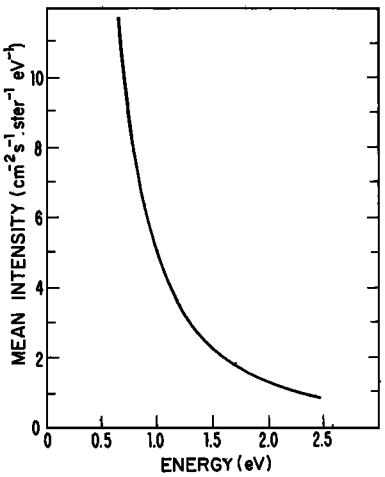

Figure 1. Energy spectrum of secondary hot oxygen atoms. The mean intensity is based on a primary source of monoenergetic O* at 2.5 eV with an intensity of 1 cm^{-2}sec^{-1}ster^{-1}. We assumed that cross sections for momentum transfer are independent of energy.

impact [*Nagy et al.*,1980], taking rates of 1.2×10^{-6} sec^{-1} and 2.4×10^{-7} sec^{-1} to apply for the early part of the Pioneer mission. The source term was adjusted (by a factor of 1.2) to allow for production of O* by

$$CO^{+} + CO_2 \rightarrow CO + CO_2^{+} \quad (9)$$

followed by

$$CO_2^{+} + O \rightarrow CO + O_2^{+} \quad (10)$$

and (1). Cross sections for momentum transfer were taken from Konowalow *et al.*[1959] and Yun and Mason [1962].

Densities of O* derived here are in good agreement with values inferred by Nagy *et al.* [1981] from analysis of the 1304Å dayglow observed by Pioneer Venus. Nagy *et al.* [1981] calculated concentrations for O* higher than our results by about a factor of 5. The discrepancy may be attributed in part to their adoption of a small cross section Q with a correspondingly lower exobase (172 km) and in part to their assumption that recombination of O_2^{+} proceeds significantly by

$$O_2^{+} + e \rightarrow O(^3P) + O(^3P). \quad (11)$$

We assumed a dominant role for (1), as indicated by Zipf [1970].

The distribution of neutral O above the plasmapause is shown as a function of solar zenith angle in Figure 3. The average location of the plasmapause was taken from Brace *et al.*[1980]. The column of thermal O above the plasmapause was calculated by combining positional data from Brace *et al.*[1980] with densities from Keating *et al.* [1980], and averaging appropriately. Distributions of O* were obtained as discussed above. Densities of O and O* are comparable, according to the results in Figure 3.

Oxygen is ionized above the plasmapause at a rate of 1.2×10^{-6} sec^{-1} due to photoionization and at a rate of about 2.2×10^{-6} sec^{-1} by electron impact in the plasmasheath. The latter is more uncertain. It was obtained using electron densities ($\approx 2 \times 10^{1}$ cm^{-3}) and temperatures ($\approx 1.4 \times 10^{6}$ °K) adapted from Spreiter and Stahara [1980] and Brace *et al.*[1980]. Cross sections for electron impact ionization of O ($\approx 1.4 \times 10^{-16}$ cm^2) were taken from Fite and Brackmann [1959]. We estimate, using the data in Figure 3, that the oxygen is ionized above the plasmapause at a planet-wide rate of 3×10^{25} atoms sec^{-1}. Ions formed in this region are swept up and removed by solar wind [*Michel*,1971]. The loss rate for O equals 6×10^{6} atoms cm^{-2}sec^{-1}, which may be compared to the rate for escape of H, 10^{7} atoms cm^{-2}sec^{-1} according to McElroy *et al.*[1982]. Escape may also occur also sporadically, as observed by Brace *et al.* [1980,1982].

The rate for removal of oxygen derived here is consistent with the upper limit on mass loading discussed by Cloutier *et al.*[1969]. The rates would be identical if the flux of unperturbed solar wind were 4×10^{8} H^{+} cm^{-2} sec^{-1} and if the effective target radius were 9000 km, values typical for conditions during the Pioneer Venus mission [*Spreiter and Stahara*, 1980]. It seems probable therefore that the dynamics of the interaction of Venus with solar wind are tuned to assure maximum mass loading of the post-shock solar plasma. The geometry of the bow shock and plasmapause should adjust to

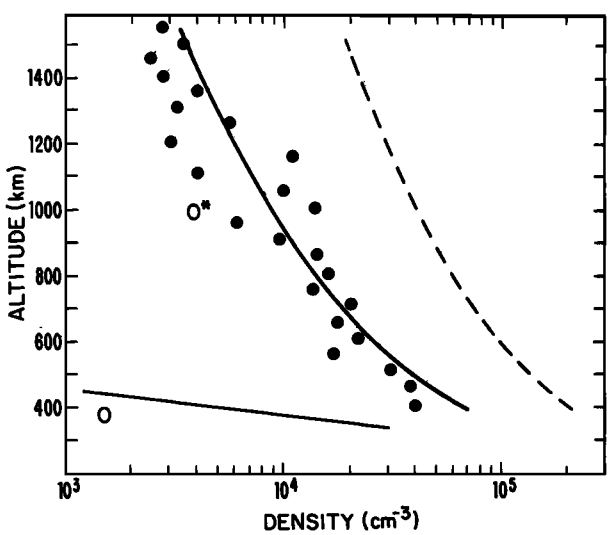

Figure 2. Oxygen densities in Venus' upper atmosphere. Calculated densities of hot oxygen (O*) are designated by the thick, solid line. Oxygen atoms emanate from an altitude of about 190 km with energy spectrum in Figure 1. The observed densities (dots) are taken from OUVS data reported by Nagy *et al.* [1981]. Nagy *et al.*'s theoretical calculations for O* are also shown (dashed line). Thermal oxygen densities (O, thin line), extrapolated from the atmospheric models of Keating *et al.* [1980], are shown for comparison.

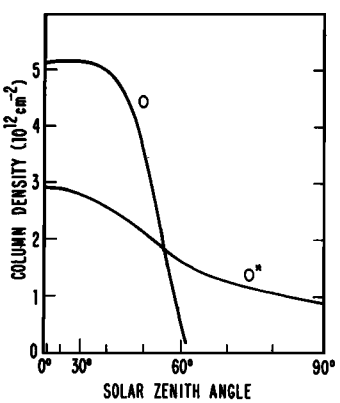

Figure 3. Column densities of neutral oxygen above Venus' plasmapause as a function of solar zenith angle. The abscissa has been scaled in accord with fractional surface area. Thermal oxygen (O) and hot atoms (O*) contribute equally to the total amount of neutral O above the plasmapause, approximately 8×10^{30} atoms.

absorb the pressure of the external solar wind and the rate for escape of O would vary proportionally.

It appears that escape of O is regulated by external influences. Escape of H, on the other hand, depends on internal conditions: supply of H to the thermosphere; the extent of vertical mixing; and various chemical reactions [*Hunten,* 1973; *Sze and McElroy,* 1975; *Kumar et al.*,1978; *Hodges and Tinsley*,1981; *McElroy et al.*,1982]. Escape of O should be comparatively constant in time. We might expect an imbalance in rates for escape of H and O to give rise to a change in the concentration of atmospheric CO. Excess escape of O would occur at the expense of CO_2 with consequent production of CO. We propose that an increase in CO would enhance the escape of hydrogen and that the stoichiometric balance of H and O would be restored accordingly. The mechanism could operate as follows.

An increase in CO would provide more effective removal of O_2 in Venus' stratosphere, thus lowering the supply of oxidant required for aerosol formation at lower altitudes [Prinn,1975]. A reduction in the concentration of hygroscopic aerosols would allow more efficient penetration of H_2O to the stratosphere, with a consequent increase in supply of H to the exosphere. The mechanism would be similarly effective in decreasing H_2O and H if escape of O were too low. Alternative mechanisms could regulate escape of H through supply of H_2 or HCl to the upper atmosphere, although the importance of these gases in supply of H is not yet clearly defined. Concentrations of H_2 and HCl in the deep atmosphere might be expected to vary in proportion to the abundance of CO (e.g., reaction **12**, below). Thus, escape of H would respond to changes in CO and vice versa.

The response of CO would occur on a time scale of 3.5×10^8 years; H would adjust much more rapidly. It appears that a mildly reducing state of Venus' atmosphere is required to supply H atoms at the rate necessary to balance escape of O. Escape of H is more efficient on Mars, and a compatible supply of H is maintained by mildly oxidizing conditions in this case.

One might expect early degassing on Venus to release materials with oxidation states similar to those for terrestrial volcanic gases, $[CO]/[CO_2] = 10^{-2}$, $[H_2]/[H_2O] = 10^{-2}$ [*Holland,* 1978]. The primitive atmosphere would be highly reducing in this case. The ratio $[CO]/[CO_2]$ would remain about 10^{-2}, but $[H_2]/[H_2O]$ would adjust in accord with the water-gas equilibrium.

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \qquad (12)$$

If the H_2O abundance were of order 10^{-2} as suggested by McElroy *et al.* [1982] the abundance of H_2 would be about 10^{-3}, assuming temperatures similar to those in the present atmosphere. Abundances of H_2 and H would be high in the upper atmosphere, and escape of H would proceed both by thermal evaporation and by ionospheric reactions involving H_2. Early escape rates for H could be as large as 4×10^8 $cm^{-2}sec^{-1}$.

In summary, Venus is losing H_2O at the present time at a rate of 6×10^6 molecules $cm^{-2}sec^{-1}$. Both H and O are lost to space, with escape of H regulated by the oxidation state of the atmosphere. Escape of H was much higher in the past, when the atmosphere was more reducing. We suggest that oxygen liberated by early escape of H was used in part to oxidize CO to CO_2, a subject which requires further attention.

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