was determined in four rocks and 16-day ^{48}V in six rocks. The concentration of ^{48}V was well correlated with the Ti concentration of the rocks, as would be expected if most of the ^{48}V was produced by solar-flare protons through the $^{48}Ti(p,n)$ reaction. From the ^{48}V content of rock 12062, which appeared to have been buried, we inferred a yield from galactic proton bombardment of about 40 ± 20 disintegrations per minute (dpm)/kg Fe.

As shown in Table 1, we determined ^{48}V quantitatively in the first two Apollo 15 samples received, 15016 and 15101. However, the results on 15016 were superior because weak components of the gamma-ray spectra of mare basalts suffer less interference from the Th and U decay series than do the spectra of lunar soil and breccia. The concentration of ^{48}V in 15016 leads to a galactic production rate for ^{48}V of 57 ± 11 dpm/kg Fe, based on an FeO concentration (*11*) of 22.6 percent. This result agrees well with our earlier estimate of 40 ± 20 dpm/kg Fe, within the experimental errors, and with the value 90 ± 45 dpm/kg determined by Honda and Arnold (*12*) for the yield of ^{48}V in the iron meteorite Aroos.

Although no intense solar flare directly preceded the Apollo 15 mission, 77.3-day ^{56}Co was detected in some of the samples. Since ^{56}Co is almost totally produced by solar-flare protons through the $^{56}Fe(p,n)$ reaction, the ^{56}Co detected in Apollo 15 samples was produced in the solar flare of 25 January 1971. No measurements of the intensity of this flare have been published, but a comparison of the present ^{56}Co concentrations with those of the Apollo 12 samples (*3*) suggests that the flare of 25 January 1971 was approximately 30 percent more intense than the well-characterized event of 3 November 1969.

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Mars: An Evolving Atmosphere

Abstract. *Photochemical reactions in the martian exosphere produce fast atoms of oxygen, carbon, and nitrogen and provide large escape fluxes of these elements. They appear to play a crucial role in the evolution of the martian atmosphere. The relative outgassing rates of H_2O and CO_2 on Mars are comparable with terrestrial values, although absolute rates for Mars are lower by a factor of 10^3. Nitrogen is a trace constituent, less than 1 percent, of the present martian atmosphere.*

We now understand that the atmospheric pressure at the surface of Mars is about 5 mb and that the atmosphere is composed mainly of CO_2, with trace amounts of H_2O and CO (*1*). We expect significant amounts of O_2 and O_3, produced as photochemical by-products of CO_2. Nitrogen is surprisingly rare. Analysis of data from Mariners 6 and 7 suggests an upper limit on the mixing ratio of N_2 relative to CO_2 (by volume) of 5 percent but indicates that the probable abundance is much less than this value (*2*). The outer atmosphere contains small amounts of atomic hydrogen, carbon, and oxygen (*2a*), and the planet is losing hydrogen by thermal evaporation at a significant rate, about 10^8 atoms cm^{-2} sec^{-1} (*3*). Some implications of these data regarding the possible evolutionary history of Mars are discussed in this report.

The escape rate of H, inferred from the Mariner data, is particularly significant. The escaping atoms are supplied at the expense of atmospheric water, dissociated by sunlight near the martian surface at an average rate of about 10^9 molecules cm^{-2} sec^{-1}. According to Hunten and McElroy (*4*), H_2O is reformed at the surface with an efficiency of about 90 percent, and approximately 10 percent of the H_2O dissociation events lead to formation of H_2. The escaping atoms are produced by reactions involving H_2, notably

$$O(^1D) + H_2 \rightarrow OH + H$$

$$CO_2^+ + H_2 \rightarrow CO_2H^+ + H$$

$$CO_2H^+ + e \rightarrow CO_2 + H$$

and photodissociation

$$h\nu + H_2 \rightarrow H + H$$

To a good approximation, the escape flux of H is proportional to the abundance of H_2. Hunten and McElroy estimate a mixing ratio, H_2 to CO_2, of order 10^{-6}.

Integrated over the age of the planet, about 5×10^9 years, the present escape rate of H would imply a loss of H equivalent to about 10^{25} molecules of H_2O per square centimeter of martian surface, enough to supply a surface pressure of H_2O equal to about 0.1 atm. By way of comparison, the total amount of H_2O evolved by Earth over geologic time corresponds to an average column density of 10^{28} molecules cm^{-2} (*5*). If O atoms released on Mars by H_2O photolysis and differential escape of H were to remain in the atmosphere they would supply an abundance of O_2 equal to the present observational limit in less than 10^5 years. We shall argue that the excess O is in fact lost to interplanetary space, the escape energy being supplied to O atoms in the exosphere by dissociative recombination of molecular ions.

The martian ionosphere, first detected by Mariner 4 (*6*), is produced by photoionization of CO_2. Its chemical composition is determined by competition between

$$CO_2^+ + O \rightarrow O_2^+ + CO \qquad (1)$$

and

$$CO_2^+ + e \rightarrow CO + O \qquad (2)$$

Reaction 1 is more efficient below about 250 km. Consequently O_2^+ is a major component of the martian ionosphere (*7*, *8*). It is removed by

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

If we specify the internal states of product species we may readily determine their kinetic energy. Reaction 2 leads to production of CO with 3 ev and O with 5.3 ev if both species are in their lowest internal energy states. Likewise reaction 3 can provide each of the product O atoms with as much as 3.5 ev in kinetic energy. Experimentally we know that the preferred path for reaction 3 favors production of one atom in the metastable ^1D level (*9*). The kinetic energy of O is consequently reduced to 2.5 ev.

Oxygen atoms can escape Mars if their energy exceeds 1.99 ev, and the comparable values for CO, C, and N are 3.49 ev, 1.49 ev, and 1.74 ev, respectively. Evidently O atoms produced in the exosphere by reactions 2 and 3 can escape if their velocity vectors are oriented in the upward hemisphere. Nitrogen atoms produced by

$$N_2^+ + e \rightarrow N + N \qquad (4)$$

and C atoms formed by

$$CO^+ + e \rightarrow C + O$$

can also escape. Their energies, again assuming ground state products, are 2.91 ev and 1.66 ev, respectively.

A model for the upper martian atmosphere, consistent with the Mariner data (*8*), is illustrated in Fig. 1. The exospheric temperature is 365°K, and following Brinkmann (*10*), we assume that the exosphere is at 200 km, and that CO_2 is the dominant exospheric constituent. A compatible model for the ionosphere is given in Fig. 2. As noted above, O_2^+ is the dominant constituent. The densities of O^+, N_2^+, and CO^+ are limited by the reactions

$$O^+ + CO_2 \rightarrow O_2^+ + CO$$
$$N_2^+ + CO_2 \rightarrow N_2 + CO_2^+$$

and

$$CO^+ + CO_2 \rightarrow CO + CO_2^+ \qquad (5)$$

We adopted rate coefficients consistent with recent laboratory data (*11*).

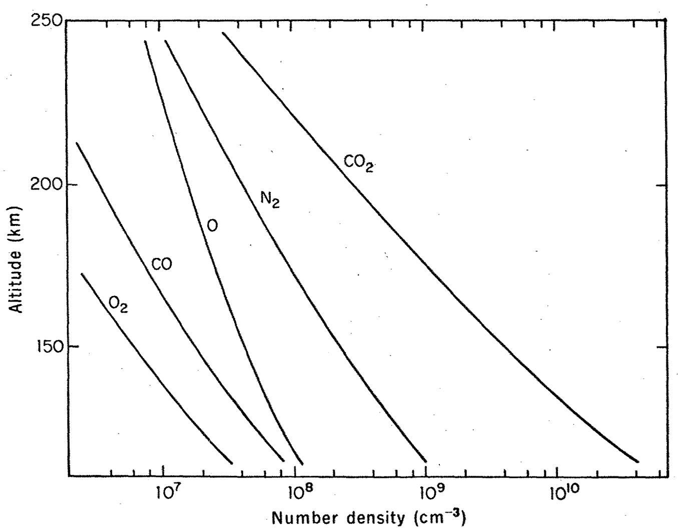
The computed escape rate for O is 6×10^7 atoms cm^{-2} sec^{-1}, averaged over the martian surface. This value is equal to approximately half the CO_2 ionization rate in the sunlit exosphere. We assumed that atoms are emitted with equal probability in the upward and downward hemispheres and allowed an additional factor of 2 to account for the absence of escaping atoms on the night side of the planet. The computed escape rate of O can balance an escape rate of H, produced ultimately from H_2O, equal to 1.2×10^8 atoms cm^{-2} sec^{-1}. This result is in excellent agreement with the number derived by Anderson and Hord (*3*) on the basis of measurements of airglow at Lyman α performed by Mariners 6 and 7.

The agreement, though unexpected, is scarcely fortuitous. We would argue that loss of H is in fact regulated by nonthermal evaporation of O. Any imbalance should lead to a rapid increase in either atmospheric CO or O_2 with a consequent change in the oxidation state of the atmosphere. Excess CO will be oxidized at the expense of photochemical products of H_2O. Dissociation of H_2O should lead therefore to a larger net yield of H_2 and consequently H. Similarly H_2O will be re-formed more efficiently in the presence of excess O_2, and the net yield of H_2 and H should be less in this case. Molecular hydrogen acts as a powerful buffer which supplies escaping atoms at precisely the rate required to maintain the present chemical balance of the atmosphere. The buffer is relatively stable. The time constant associated with H_2 is about 10^3 years (*4*) in contrast with the rather short time constants, 2 years, associated with CO and O_2 (*12*).

Nitrogen loss by reaction 4 is also efficient. With an assumed mixing ratio of 10^{-2} for N_2 in the lower atmosphere we calculate an average escape rate for N atoms equal to 3×10^5 cm^{-2} sec^{-1} (*13*). If we make the foregoing assumptions, the atmosphere would lose essentially all its nitrogen in less than 5×10^9 years. If we assume that the atmosphere evolved by rapid outgassing at an early phase in the planet's history, the time evolution of the N_2 mixing ratio, ρ, will be given by

$$\rho(t) = \rho_0 \exp\left(-\frac{4.5 \times 10^{14}}{N}\, t\right)$$

Here ρ_0 is the initial value of the mixing ratio, N is the total column density of CO_2 (cm^{-2}), and t is elapsed time measured in years. Taking $N = 2 \times 10^{23}$, its present value, we find that the N_2 mixing ratio will be reduced by a factor 10^5 in 5×10^9 years, because of recombination escape. On the other hand, if outgassing occurred at a steady rate over geologic time, then



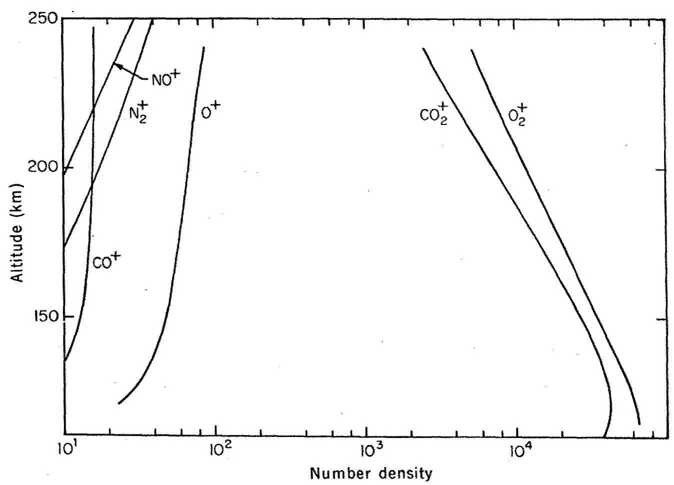


Fig. 1 (left). Number densities of CO_2, N_2, O, CO, and O_2. The turbopause is at 90 km, and the mixing ratio of N_2 in the lower atmosphere is 1 percent. Fig. 2 (right). Model for the martian ionosphere. The solar zenith angle is taken as 27°.

dynamic equilibrium would imply a mixing ratio approximately equal to 10 percent of the ratio of outgassing rates, N_2 to CO_2. If we adopt Rubey's (*5*) classic estimate for this ratio on Earth, 3×10^{-2}, and assume that it applies also to Mars, we estimate that the present mixing ratios of N_2 should be about 3×10^{-7}, with rapid outgassing, or 3×10^{-3} if outgassing occurred at a slow uniform rate (*14*).

Recombination of exospheric CO^+ supplies an escape rate of C equal to 1.5×10^5 atoms cm^{-2} sec^{-1}. In 5×10^9 years this loss would reduce the present CO_2 level of the atmosphere by about 10 percent. It is instructive to consider alternate escape mechanisms.

We note the following processes

$$h\nu + CO_2 \rightarrow C + O + O \qquad (6)$$

$$h\nu + CO \rightarrow C + O \qquad (7)$$

$$e + CO_2 \rightarrow e + C + O + O \qquad (8)$$

$$e + CO \rightarrow e + C + O \qquad (9)$$

The hot electrons in reactions 8 and 9 are supplied by photoionization of CO_2. The rates for reactions 6 to 9 may be characterized by first-order rate coefficients, J_{6-9}. From the data developed by McElroy and McConnell (*7*), the following values (sec^{-1}) can be estimated for production of C, with sufficient energy to escape from Mars:

$$J_6 = 1.4 \times 10^{-9};\ J_7 = 5.4 \times 10^{-8};$$

$$J_8 = 1.7 \times 10^{-9};\ J_9 = 5.0 \times 10^{-8}$$

The net escape rate is 6×10^5 atoms cm^{-2} sec^{-1} with approximately equal contributions from CO and CO_2. The contribution from CO_2 could be somewhat larger if significant numbers of atoms were produced in their ground states (*7*). Combining contributions from reactions 5 to 9, we calculate that the net loss of C in 5×10^9 years would be equal to 50 percent of the C now present as CO_2.

Dissociative recombination of $CO_2{}^+$ according to

$$CO_2{}^+ + e \rightarrow C + O_2$$

can also supply escape energy to C atoms. Its rate coefficient is unknown, however. If we adopt the upper limit estimated by McElroy and McConnell (*7*), 10^{-8} cm^3 sec^{-1}, we calculate associated C loss equal to 4×10^5 atoms cm^{-2} sec^{-1}.

Additional escape mechanisms have been discussed: Brinkmann (*10*) first drew attention to the possible role of photochemistry. He concluded that predissociation of N_2 could provide a significant flux of N atoms. His calculation suggests an escape rate equal to about 30 percent of the rate derived here. He mentioned the possible role of dissociative recombination but did not offer any estimates for its efficiency. Cloutier *et al.* (*15*) discussed the possible role of solar wind as a scavenging agent for atmospheric gas near the limbs of the planet. Photoions, produced near the planetary limbs, would be swept up by the $\mathbf{v} \times \mathbf{B}$ electric field generated by the impinging wind. This process may be assumed to be effective above about 250 km. The consequent escape of CO_2 could be as large as 5×10^5 molecules cm^{-2} sec^{-1}, and the corresponding escape rate for N would be 4×10^7 ρ cm^{-2} sec^{-1} where ρ is the mixing ratio of the N_2 in the lower atmosphere. The solar wind could be comparable to dissociative recombination as a sink for N.

It is of interest to compare the relative outgassing rates for H_2O and CO_2 on Mars with values for Earth. The outgassing ratio of H_2O to CO_2 (measured in numbers of molecules) is 45 for Earth (*5*). If we assume that all of the C that has entered the martian atmosphere during the past 5×10^9 years is still present, mostly as CO_2, and further assume that the present rate of H escape provides a measure of the rate at which H_2O has entered the atmosphere over the same period, then the ratio of H_2O to CO_2 evolved on Mars is also about 45. The various escape mechanisms for C could reduce the martian ratio by about a factor of 2.

In summary, dissociative recombination of $O_2{}^+$ in the martian exosphere provides an escape flux of O which balances thermal evaporation of H, produced at the expense of H_2O. This balance is a necessary consequence of water photochemistry. Dissociative recombination of exospheric $N_2{}^+$ insures that N_2 should be a minor constituent in the present martian atmosphere. A measurement of its abundance should provide important clues as to the mode of outgassing, whether it proceeded rapidly at an early phase in the planet's history or slowly over geologic time. The relative outgassing rates for H_2O and CO_2 on Mars are comparable with relative rates for Earth. However, the total amount of H_2O evolved per unit surface area of Mars is less than that for Earth by a factor of 10^3.

The chemically induced escape mechanisms discussed above are not important for Earth and Venus. The escape velocities for these planets are 11 km sec^{-1} and 10 km sec^{-1}, respectively, and escape energies are consequently about four times larger than values discussed here for Mars. Chemically induced escape will, however, play some role for Mercury and the moon.

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13. This result assumes that recombination of $N_2{}^+$ can produce two atoms with escape energy. Clearly this will be the case for ground state products, and is probably true also for recombination leading to production of $N(^4S)$ and $N(^2D)$, if one considers internal excitation of $N_2{}^+$ and allows for its thermal energy as discussed by Brinkmann (*10*). The uncertainty in product species is unlikely to modify our conclusions. The average escape rate for N may be larger than we imply since my calculations were carried out with values for the solar extreme ultraviolet flux appropriate for minimum solar activity.
14. It was assumed that the turbopause for N_2 is at 90 km, an appropriate height if the average value of the eddy diffusion coefficient is about 5×10^6 cm^{-2} sec^{-1}, which happens also to be the terrestrial value. Brinkmann (*10*) made a similar assumption, and our results for N escape are directly comparable with his. However, the Mariner data suggest that eddy coefficients in the present martian atmosphere may be as large as 5×10^8 cm^{-2} sec^{-1}, and the turbopause could be as high as 140 km (*12*). If this situation prevailed over geologic time, the magnitude of the N escape flux would be reduced by about a factor 4.2, and the exponent in the expression for $\rho(t)$ should be lowered accordingly. The distinction between rapid and uniformly outgassing models is thus reduced. With rapid outgassing we would estimate a current mixing ratio of N_2 equal to 0.2 percent. With uniform outgassing the number is about five times larger. Other conclusions in this report are insensitive to assumptions regarding the magnitude of the eddy coefficient.
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