mately 50 percent of the primary peak. The residual exhibits a scale height similar to N_2, and is tentatively attributed to NO.

The enrichment in ^{15}N may arise as a result of preferential escape of ^{14}N from the upper atmosphere. Diffusive separation above the turbopause will act to enrich the upper atmosphere in ^{14}N. Escape proceeds by production of fast nitrogen atoms in the exosphere, either through dissociative recombination of N_2^+ (*5*), or through electron impact dissociation of N_2 (*6*). A relatively simple analysis should suffice to define a lower bound to the initial abundance of N_2 (*7*).

We introduce a parameter R to indicate the extent to which the exosphere may be depleted in ^{15}N owing to diffusive separation at lower altitudes:

$$R = f_c(t)/f_0(t) \quad (1)$$

where $f_c(t)$ denotes the mixing ratio of ^{15}N relative to ^{14}N at the exobase in the present atmosphere—that is, at time t, with $f_0(t)$ the analogous quantity for the bulk atmosphere. The parameter R is a function of the value assumed for the eddy diffusion coefficient in the upper atmosphere, as discussed, for example, by McElroy and Yung (*7*). The enrichment of the present atmosphere in ^{15}N with respect to its initial condition is given by

$$\mathscr{E}(t) = f_0(t)/f_0(0) \quad (2)$$

and it may be readily shown that:

$$\mathscr{E}(t) = [\mathscr{N}(0)/\mathscr{N}(t)]^{1-R} \quad (3)$$

where $\mathscr{N}(0)$ denotes the initial abundance of N_2, and $\mathscr{N}(t)$ indicates the present abundance. The relation given by Eq. 3 assumes an initial reservoir of N_2 which is modified by subsequent escape. It assumes, explicitly, a passive role for the surface and ignores therefore the possibility that nitrogen might be incorporated in surface minerals, as discussed, for example, by Yung *et al.* (*6*). A surface sink would lead to a smaller value for $\mathscr{E}(t)$ or, equivalently, it would imply a larger value for $\mathscr{N}(0)$ corresponding to any particular choice of $\mathscr{E}(t)$.

Values for $\mathscr{N}(0)$ are shown in Fig. 2, for several values of the enrichment factor $\mathscr{E}(t)$, as a function of the magnitude for the eddy diffusion coefficient in Mars' upper atmosphere. The Viking results appear to indicate a diffusion coefficient near 10^8 cm^2 sec^{-1}, consistent with previous analyses (*8*). We assume that $f_0(0)$ should have a value equal to that for Earth, a reasonable assumption in view of results noted earlier for the isotopes of carbon and oxygen. It would be difficult to escape the conclusion that Mars at some past time must have contained an abundance of N_2 equivalent to a partial pressure of at least 2 millibars.

A similar analysis for the oxygen isotopes would imply an exceedingly large source of oxygen (*6*). An enrichment of less than 3 percent in ^{18}O would require exchange between the atmosphere and a subsurface reservoir, either CO_2 or H_2O, which must contain an abundance of these compounds equivalent to an atmospheric pressure of at least 2 bars.

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3. Errors given throughout this report are the standard deviations in the averages of the approximately six values from which the averages are calculated in each case. For purposes of computation, it was assumed that diffusive equilibrium existed above 125 km. Before averaging, the individual ratios were corrected to allow for depletion of the heavier molecules with altitude. The averages should thus fall near the values expected in the bulk atmosphere.
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9. Work at the University of Minnesota and at Harvard University was supported by NASA under contracts NAS-1-9697 and NAS-1-10492, respectively. A.O.N. is indebted to Ward Johnson for help in making computations.

2 September 1976

Isotopic Composition of Nitrogen: Implications for the Past History of Mars' Atmosphere

Abstract. *Models are presented for the past history of nitrogen on Mars based on Viking measurements showing that the atmosphere is enriched in* ^{15}N. *The enrichment is attributed to selective escape, with fast atoms formed in the exosphere by electron impact dissociation of* N_2 *and by dissociative recombination of* N_2^+. *The initial partial pressure of* N_2 *should have been at least as large as several millibars and could have been as large as 30 millibars if surface processes were to represent an important sink for atmospheric* HNO_2 *and* HNO_3.

Nitrogen accounts for about 2.5 percent of the present martian atmosphere (*1*). It is clear, however, that the concentration of nitrogen on Mars must have been much higher in the past. The heavy isotope, ^{15}N, is enriched in the present atmosphere by about 75 percent relative to a terrestrial standard (*2*). In contrast, the relative abundances of oxygen and carbon isotopes on Mars appear to be similar to values observed for the earth (*1, 2*). It is hard to escape the conclusion that Mars must have lost an appreciable amount of N_2 to space over the past 4.5×10^9 years. The initial abundance of N_2 may have been large enough to provide an atmospheric partial pressure of at least several millibars (*2*).

Escape of nitrogen from Mars may proceed by production of fast atoms in the exosphere, by either dissociative recombination of N_2^+ (*3*)

$$N_2^+ + e \rightarrow N + N \quad (1)$$

or electron impact dissociation of N_2 (*4*)

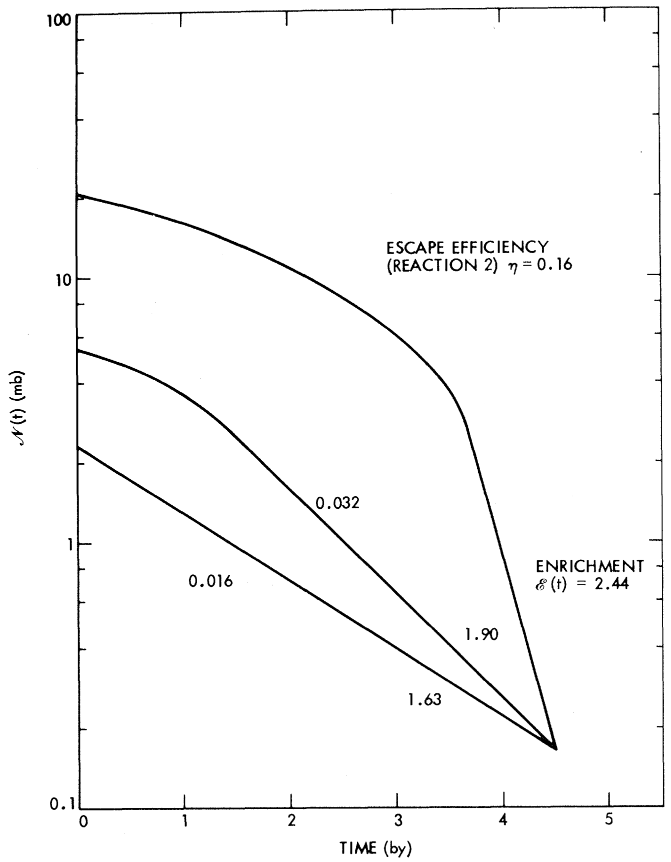
$$e + N_2 \rightarrow e + N + N \quad (2)$$

or predissociation of N_2 (*5*)

$$h\nu + N_2 \rightarrow N + N \quad (3)$$

It appears that the source should be dominated by a combination of reactions 1 and 2. The escape flux due to reaction 1 will be a fairly sensitive function of the value assumed for the partial pressure of CO_2, since N_2^+ ions are removed mainly by charge transfer to CO_2. Loss of nitrogen due to reaction 2 is proportional to the mixing ratio for N_2, at least for small values of this parameter.

According to Michels (*6*), reaction 1 involves production of both N(^4S) and N(^2D) in approximately similar amounts. If we assume that ion and electron temperatures in Mars' exosphere should have values near 400°K, we may compute an average speed for atoms formed by reaction 1 of magnitude 4.96 km sec^{-1}. The initial velocities for ^{15}N should be adjusted by a factor of 0.95 in order to allow for the heavier mass of the less abundant isotope. The velocity required to escape Mars' gravitational field from an altitude of about 210 km above the planetary surface is 4.68 km sec^{-1}. It would appear that the escape rate for reaction 1 should have magnitude approximately equal to the integrated rate for recombination of N_2^+ above the exobase (*7*).



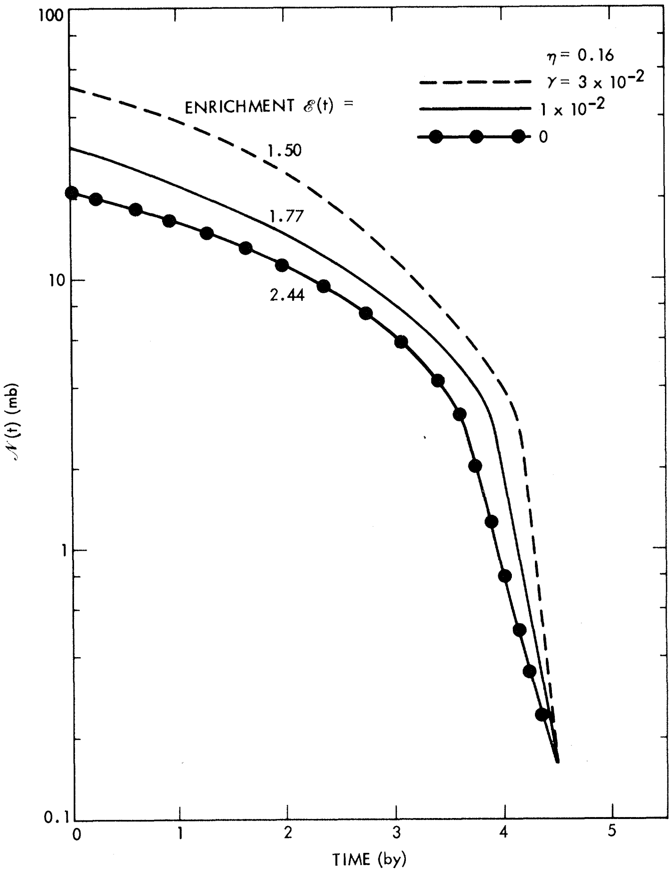
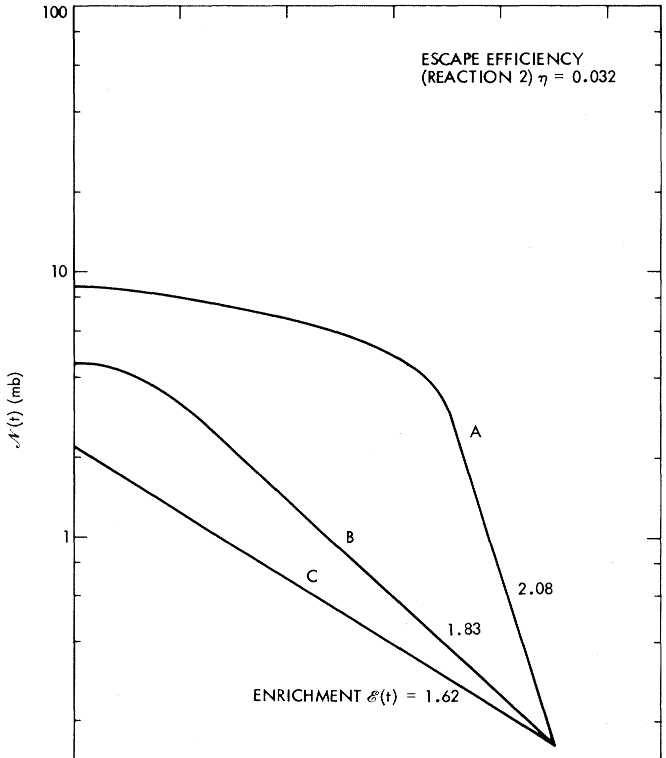


Fig. 1 (left). Abundance of N_2 (in millibars) as a function of time (in units of 10^9 years). The escape efficiencies for reaction 2 were assumed to be 0.16, 0.032, and 0.016, respectively. The corresponding enrichment factors at time $t = 4.5$ billion years are 2.44, 1.90, and 1.63, respectively, for an eddy diffusion coefficient $K = 3 \times 10^8$ cm^2 sec^{-1}. Fig. 2 (right). Abundance of N_2 (in millibars) as a function of time (in units of 10^9 years). The escape efficiency for reaction 2 was assumed to be 0.16. Results are shown for heterogeneous reactivity coefficients (for HNO_2 and HNO_3) $\gamma = 3 \times 10^{-2}$, 1×10^{-2}, and 0. Corresponding enrichment factors at time $t = 4.5$ billion years are 1.50, 1.77, and 2.44, respectively, for $K = 3 \times 10^8$ cm^2 sec^{-1}.

We expect that the dominant path for electron impact dissociation of N_2 should also involve production of $N(^2D)$ and $N(^4S)$. Production of atoms with sufficient energy to escape Mars would require that the target molecules be raised to internal states with energies at least 15.6 ev above the molecular ground state. A significant yield for fast N would not be expected if the molecules were excited to internal states with energies above 19 ev: autoionization should represent the dominant reaction path in this case (*8*). We are therefore concerned primarily with excitation of N_2 to internal states with energies in the range 15.6 to 19 ev. Strobel (*9*), using oscillator strengths measured by Wight *et al.* (*8*), estimates that approximately 16 percent of all dissociative reactions (reaction 2) might result in production of atoms with velocities sufficient for escape. His result is adopted as a guide for the analysis presented below.

We first consider a model in which the surface is taken to be passive—that is, a model in which we explicitly ignore the possibility that appreciable quantities of nitrogen might be removed from the at-

Fig. 3. Abundance of N_2 (in millibars) as a function of time (in units of 10^9 years). The escape efficiency for reaction 2 was assumed to be 0.032. Curve A represents results for the case in which the atmospheric CO_2 pressure was assumed to fall below 0.65 mbar for one-third of a climatic cycle. Curves B and C represent results for the cases in which the CO_2 pressure rises to 65 mbar for one-third and one-tenth of a climatic cycle, respectively. The enrichment factors at time $t = 4.5$ billion years for curves A, B, and C are 2.08, 1.83, and 1.62, respectively, for $K = 3 \times 10^8$ cm^2 sec^{-1}.



mosphere by irreversible heterogeneous processes at the surface (*4*). We assume that the concentration of atmospheric CO_2 remains constant with time and use the model described by McElroy and Yung (*10*) to evaluate the past evolutionary history of N_2. Results are shown in Fig. 1 for η, the efficiency with which escaping atoms may be formed by reaction 2, equal to 0.16, 0.032, and 0.016; that is, with the efficiency taken equal to the value given by Strobel (*9*) and reduced by factors of 5 and 10, respectively. This leads to predicted values for the enrichment of ^{15}N equal to 144, 90, and 63 percent, respectively; that is, the ratio $^{15}N/^{14}N$ exceeds the terrestrial value by factors of 2.44, 1.90, and 1.63, respectively. A model with an efficiency of 0.03 would be consistent with the Viking measurements. The initial concentration of N_2 would correspond to a partial pressure of about 5 mbar in this case. The contributions to the escape flux due to reactions 1 and 2 are comparable for an efficiency of 0.032.

Figure 2 shows results obtained with a model in which we allowed for incorporation of HNO_2 and HNO_3 into surface minerals, with the heterogeneous reaction coefficient, γ, taken equal to 3×10^{-2}, 1×10^{-2}, and 0 (*4*). For all cases shown in Fig. 2 we used the efficiency factor η given by Strobel (*9*). A reaction coefficient γ equal to 10^{-2} provides a satisfactory fit to the Viking data, and would imply an initial partial pressure of N_2 equal to about 30 mbar. The model requires a net integrated deposition of nitrogen in minerals of magnitude 2.5×10^{23} atoms (N) per square centimeter averaged over the martian surface. The escape rate for nitrogen is dominated by reaction 2 for all models shown here.

Figure 3 shows results obtained with a model in which we allow for a secular variation in the partial pressure of atmospheric CO_2, which might arise because of changes in the obliquity and orbital eccentricity of Mars if the atmospheric pressure were controlled by an equilibrium with the polar ice cap, as discussed for example by Ward *et al.* (*11*). Curve A is based on the assumption that the partial pressure of CO_2 was equal to 10 percent of the present value for approximately 30 percent of the time over the past 4.5×10^9 years. Curves B and C model the case for which the pressure might have been much higher in the past: the partial pressure of CO_2 is taken as 65 mbar, for 33 percent of the time in curve B and for as much as 10 percent of the time in curve C (*12*). For the model in Fig. 3 we assumed a passive surface, $\gamma = 0$, and $\eta = 0.032$. The initial partial pressure of N_2 for all three cases lies in the range 2 to 9 mbar.

The measurement of enriched ^{15}N on Mars provides a powerful diagnostic tool which may be used to derive invaluable data on the past history of Mars. The uncertainty indicated by the spread of results shown in Figs. 1 to 3 may be narrowed considerably by careful laboratory studies of the velocity distribution of atoms formed by electron impact dissociation of N_2. An appropriate laboratory investigation would clarify the role that heterogeneous processes might play in the chemistry of nitrogen on Mars and would permit a quantitative estimate of the rate at which nitrogen may have been incorporated in surface minerals over the past 4.5×10^9 years. It is difficult, in any event, to escape the conclusion that the abundance of atmospheric nitrogen on Mars must have been much higher in the past: the partial pressure of the gas may have been as high as 30 mbar, and was surely no less than about 2 mbar.

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7. We assume here that atoms are released isotropically. Half of the atoms formed will be emitted in the upward hemisphere and may escape to space without suffering further collisions. We use a model atmosphere given in (*4*) to describe mean martian conditions. The model has an exobase at 210 km. It is interesting to note that reaction 1 could provide a selective mechanism for escape of ^{14}N, although for most models considered here nitrogen is lost by reaction 2 rather than reaction 1, and one would not expect the escape efficiency for reaction 2 to depend critically on isotopic composition. Moreover, the temperature assumed here for ions may be conservative on the low side, which would further reduce the dependence of the escape flux on the isotopic composition of N_2. We shall assume that ^{15}N and ^{14}N should escape with equal probability from the exobase. Clearly this matter should be reexamined as further data become available on the detailed kinetics for reactions 1 and 2, and as further measurements are made to define the temperature of Mars' high-altitude ionosphere. If we were to neglect the escape flux due to reaction 2 and if we were to further postulate that reaction 1 should favor escape of ^{14}N by a factor of 2, the initial pressure of N_2 would be 0.56 mbar and the enrichment for ^{15}N would be about 110 percent for a passive surface. If we were to reduce the escape efficiency for reaction 2 to a value $\eta = 0.008$, and again assume that reaction 1 favors reduction of fast ^{14}N by a factor of 2, the enrichment for ^{15}N would be about 140 percent, and the initial N_2 pressure would have a value of 1.1 mbar, for models similar to Fig. 1.
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13. Supported by NASA contracts NAS-1-9697 and NAS-1-10492 to the University of Minnesota and Harvard University, respectively.

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Search for Organic and Volatile Inorganic Compounds in Two Surface Samples from the Chryse Planitia Region of Mars

Abstract. *Two surface samples collected from the Chryse Planitia region of Mars were heated to temperatures up to 500°C, and the volatiles that they evolved were analyzed with a gas chromatograph–mass spectrometer. Only water and carbon dioxide were detected. This implies that organic compounds have not accumulated to the extent that individual components could be detected at levels of a few parts in* 10^9 *by weight in our samples. Proposed mechanisms for the accumulation and destruction of organic compounds are discussed in the light of this limit.*

The objective of the Viking molecular analysis experiment is to analyze periodically the composition of the atmosphere at the surface of Mars and to search for organic compounds and certain inorganic volatiles in the surface material at the landing site. The principal instrument used for both investigations is a mass spectrometer (MS). It is used in conjunction with a gas chromatograph (GC) for the organic analyses. The objective of the entire system have been described previously (*1*), as have the results of the atmospheric analyses (*2*).

A gas chromatograph–mass spectrometer (GCMS) was chosen for the search for organic compounds chiefly because of its sensitivity and versatility. A number of mechanisms could contribute to the contemporary accumulation of organic compounds on Mars, for example, photochemical or biological processes and