



Isotopic Composition of the Martian Atmosphere

Alfred O. Nier; Michael B. McElroy; Yuk Ling Yung

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in B2, being smaller than those in B3, were better covered by the bigger dunes apparent in the B2 pictures, and that the smaller dunes in B3 might not cover the ejecta from the larger craters there as well. Site B3 was favored by still others independent of the dune argument since it appeared to them that B3 was smoothed by uniform mantling.

In the B sites, where dunes and aeolian mantle were observed, an attempt was made to estimate thickness of cover based on dune spacing and dune slopes. The minimum thickness was estimated as being adequate to cover small crater ejecta. Estimating impact crater ejecta block size at two crater diameters from the crater Mie (100 km in diameter) was difficult. The estimated 10-m block size was based on ejecta sizes measured in the Surveyor 7 landing site and Apollo 15, Apollo 16, and Apollo 17 high-resolution photographs. The block populations depend on the number of small craters below the resolution limit that may excavate blocks from below the wind-laid mantle and the number exposed by deflation. Slopes were deemed as acceptable based on Earth analogs, except on the inner margins of craters.

The infrared thermal mapper results for the B2 region indicated low thermal inertia and large amounts of fines (4). No data were available for the specific candidate ellipses. The thermal inertia at B3 was determined to be approximately similar to that at the Viking 1 site; the required noon coverage was not available (4).

Observations showed more atmospheric water at B2 than at B3 (2). There was a greater diurnal variation in water content at B2 and it had an assumed 10° warmer surface temperature, although no data were available at the site.

These factors were carefully weighed; and the B3 site was selected for the following reasons.

1) *Safety*. It appears that B3 is adequately mantled, muted, and filled. Site B2 may be as good, but the seeing due to clouds and imaging quality diminishes confidence in the coverage. Site B3 appears more homogeneous throughout the area of the 99 percent ellipse.

2) *Science*. There is a small distinction between the sites. The warmer temperature at B2 is in its favor. The water content difference was not deemed significant. The most significant scientific distinction had already been realized when the northern latitude band was selected.

3) *Operations*. Implementation is straightforward at B3. The additional data analysis and acquisition required to

land at any other site could result in a landing delay and significant additional operational complexity. Acceptance of this additional complexity was not justified, based on the B3 assessment cited above.

Subsequently, the B3 α and β ellipses (Fig. 8) were coalesced into one with preliminary coordinates of 48°N, 226°W. Final coordinates (47.89°N, 225.86°W) were selected on 30 August after review of the rev 20 stereoscopic coverage. Detailed mosaic of the landing site with the lander dispersion ellipse is given in Fig. 10.

The crater Mie east of the landing point is covered with larger dunes and deflation hollows (Fig. 11), and the polygonally fractured lava flows west of the site (Fig. 12) are covered with a thin mantle of wind-blown material that partially fills the fractures. At the south end of the B3 region, a large channel (Fig. 13) dissects and crosses the area, extending 600 km to the south toward the Elysium volcanoes. Some of the large craters (Fig. 14) are extensively modified by wind erosion, possible water sapping, and dissection, so that their ejecta blankets are etched out in negative relief. The area is thus partially mantled by aeolian material in the north, where the landing site is located, and stripped in the south. The crater counts previously cited confirm this interpretation.

The conclusion of the search for the Viking 2 site was the selection of the B3 site in Utopia Planitia. The landing was successfully accomplished at 3:58:20 p.m. P.D.T., earth received time, on 3 September 1976.

Studies are under way to compare the actual conditions encountered at both the Viking 1 and Viking 2 landing sites with those expected on the basis of the

prelanding observations. These results will be reported on when completed. Tentatively, Viking 2 rests in a deflation hollow.

H. MASURSKY

U.S. Geological Survey,
Flagstaff, Arizona 86001

N. L. CRABILL

NASA Langley Research Center,
Hampton, Virginia 23665

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2. C. B. Farmer, personal communication.
3. G. Schaber, J. Boyce, A. Dial, M. Strobell, and G. Stewart provided near-real-time crater counting and analyses for these and many other locations.
4. H. Kieffer, personal communication.
5. The Viking 2 site certification effort was a team effort as it was for the Viking 1, except that infrared observations rather than radar data were used in conjunction with images to evaluate the sites. H. H. Kieffer and his associates reduced infrared thermal mapper data and made them available in near real time to help in site evaluation. C. B. Farmer and his team similarly reduced the Mars atmospheric water data very expeditiously. Hazard analyses were done by J. A. Cutts, K. W. Farrell, L. Crumpler, T. Spudis, and E. Theilig. Geological and terrain analyses were performed by J. E. Guest, R. Greeley, G. Schaber, J. Boyce, J. A. Cutts, K. W. Farrell, M. H. Carr, and L. Soderblom. Image data processing proceeded through a complicated chain with the help of R. Johansen, M. Martin, and associates at the Mission and Test Imaging System Facility; G. Traver and associates at the Mission and Test Photoprocessing System; R. Ruiz and associates at the Image Processing Laboratory; J. Hewitt and associates at the JPL photo laboratory; and R. Tyner and W. Sowers (who made photographic mosaics as fast as these images were delivered). L. B. Garrett and others organized this image processing system; and D. Roos monitored its day-to-day implementation. Thanks are also due to M. J. Alazard, D. L. Anderson, G. A. Briggs, D. M. Davies, J. D. Goodlette, R. Hargraves, S. L. Hess, L. Kingsland, T. Z. Martin, W. H. Michael, H. J. Moore, II, E. C. Morris, T. A. Mutch, F. T. Nicholson, W. J. O'Neil, T. Owen, F. D. Palluconi, J. D. Porter, R. J. Reichert, C. Sagan, R. W. Sjoström, B. A. Smith, C. W. Snyder, G. A. Soffen, T. E. Thorpe, P. Toulmin III, E. D. Vogt, and the rest of the Viking Flight Team at Jet Propulsion Laboratory and the U.S. Geological Survey at Flagstaff. As before, J. S. Martin, Jr., A. T. Young, and B. G. Lee provided a ready hand at the Viking tiller.

2 September 1976

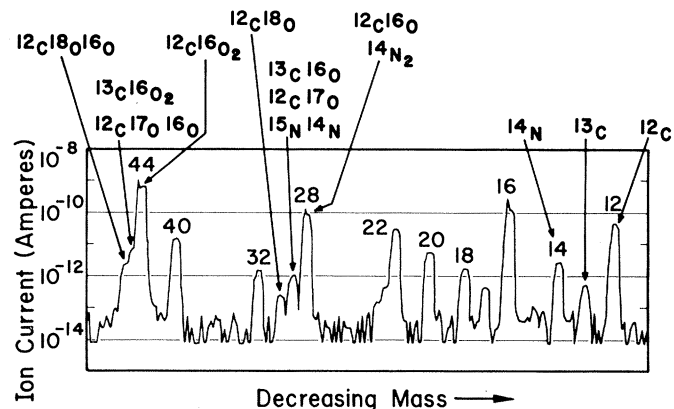
Isotopic Composition of the Martian Atmosphere

Abstract. Results from the neutral mass spectrometer carried on the aeroshell of Viking 1 show evidence for NO in the upper atmosphere of Mars and indicate that the isotopic composition of carbon and oxygen is similar to that of Earth. Mars is enriched in ^{15}N relative to Earth by about 75 percent, a consequence of escape that implies an initial abundance of nitrogen equivalent to a partial pressure of at least 2 millibars. The initial abundance of oxygen present either as CO_2 or H_2O must be equivalent to an exchangeable atmospheric pressure of at least 2 bars in order to inhibit escape-related enrichment of ^{18}O .

Viking 1, which landed on Mars on 20 July 1976, included as part of its scientific payload a mass spectrometer designed to measure properties of the neutral atmosphere between about 100 and 200 km during the descent of the spacecraft to

the planet's surface (1). A preliminary account of the results has been published (2). The martian atmosphere consists mainly of CO_2 , with traces of N_2 , Ar, O_2 , CO, and O. The relative abundances of oxygen and carbon isotopes in the mar-

Fig. 1. Mass spectrum showing various mass peaks (amu) as spectra are scanned. Since time also increases to the right (5 seconds per scan), the spectrum includes a distortion due to the increase in ambient pressure during the time of a spectral scan. Thus, for example, the 12-amu peak due to ^{12}C from CO_2 is 1.4 times higher, when referred to the 44-amu peak, than it would have been had the spectrum been scanned at constant altitude. In all of the results reported here, ion peak magnitudes within a particular spectrum are corrected to the values they would have had at the time of the start of the spectral scan. Peaks such as those at 46 and 45 amu, while not resolved in the sense that there is a valley between adjacent peaks, have essentially flat tops, showing that there is little interfering background from the large neighboring peak 44 included. They may thus be used in computing isotopic mixing ratios.



tian atmosphere were observed to be similar to values measured for the terrestrial atmosphere, although quantitative results could not be presented in the preliminary report. An updated account of the analysis is given here, with emphasis on isotopic composition. We report results for the ratios $^{18}\text{O}/^{16}\text{O}$, $^{13}\text{C}/^{12}\text{C}$, and $^{15}\text{N}/^{14}\text{N}$. We describe also evidence for a tentative identification of NO and note briefly some implications for the past evolutionary history of martian volatiles.

The analysis given here is based on six spectra taken over the height range 111 to 157 km. Data at lower altitude are of relatively limited use for present purposes, because of pressure smearing of individual mass peaks. Mass peaks in spectra taken at higher altitude are too small for accurate measurement of the less abundant isotopes. A typical spectrum for an altitude of 133 km is shown in Fig. 1. The ratio $^{18}\text{O}/^{16}\text{O}$ may be inferred either from the peaks at 46 and 44, or from the peaks at 23 and 22. The peaks due to singly charged CO_2 , 46 and 44, indicate an isotopic ratio, $^{18}\text{O}/^{16}\text{O}$, equal to 0.0020 ± 0.0001 (3). The peaks due to doubly charged CO_2 suggest a ratio equal to 0.0021 ± 0.0002 . These results may be compared to the average terrestrial ratio (4) of 0.00204. It is clear that the martian atmosphere cannot be enriched to any appreciable extent in ^{18}O relative to Earth. The enrichment cannot exceed 13 percent and is most probably less than about 3 percent.

Similar conclusions apply for ^{13}C . The ratio $^{13}\text{C}/^{12}\text{C}$ may be derived from a study of peaks at 45 and 44 or from peaks at 13 and 12. In principle, the ratio should be given also from peaks at 22.5 and 22. Ratios derived from the 22.5 and 22 peaks are anomalous, however, both in the martian spectra and in spectra taken with two similar instruments in the laboratory. The anomaly may be due to a lack of mass resolution in the instrument or to a peculiarity in the ionization process,

which might result in an enrichment of the signal due to $(^{13}\text{C}^{16}\text{O}_2)^{2+}$. (This matter will be investigated further.) The peaks at 45 and 44 indicate a $^{13}\text{C}/^{12}\text{C}$ ratio of 0.0115 ± 0.0003 . The peaks at 13 and 12 give a value of 0.0115 ± 0.0004 . These results may be compared to the average terrestrial value of 0.0112 (4). The enrichment in ^{13}C for the martian atmosphere cannot exceed 5 percent, and is most probably less than 2 percent.

Peaks at 28 and 29 include contributions due to both N_2^+ and CO^+ , with the latter formed mainly in the instrument by dissociative ionization of CO_2 . For the altitude range discussed here, approximately one-third to one-half of the signals at 28 and 29 may be attributed to N_2^+ . The exact amounts depend on the altitude and are determined from the mass peaks 44, 14, and 12 and from the laboratory calibrations giving the CO_2

and N_2 fragmentation patterns. After correction for CO^+ , with carbon and oxygen isotopic compositions being measured independently, as noted above, we deduce a ratio $^{15}\text{N}/^{14}\text{N}$ of magnitude 0.0064 ± 0.001 for the bulk atmosphere. This may be compared to the terrestrial value of 0.00368 (4). There can be little doubt that the martian atmosphere is enriched in ^{15}N relative to Earth by about 75 percent. The enrichment may be clearly seen in all six spectra adopted for critical study in our investigation.

The peak at mass 30 contains a contribution due to $(^{12}\text{C}^{18}\text{O})^+$, whose magnitude may be readily estimated from known calibration parameters for the instrument, and concentrations for CO independently set by careful analysis of the peaks at 46, 44, 28, and 12. After correcting for $(^{12}\text{C}^{18}\text{O})^+$, we find a residual at mass 30, of magnitude equal to approxi-

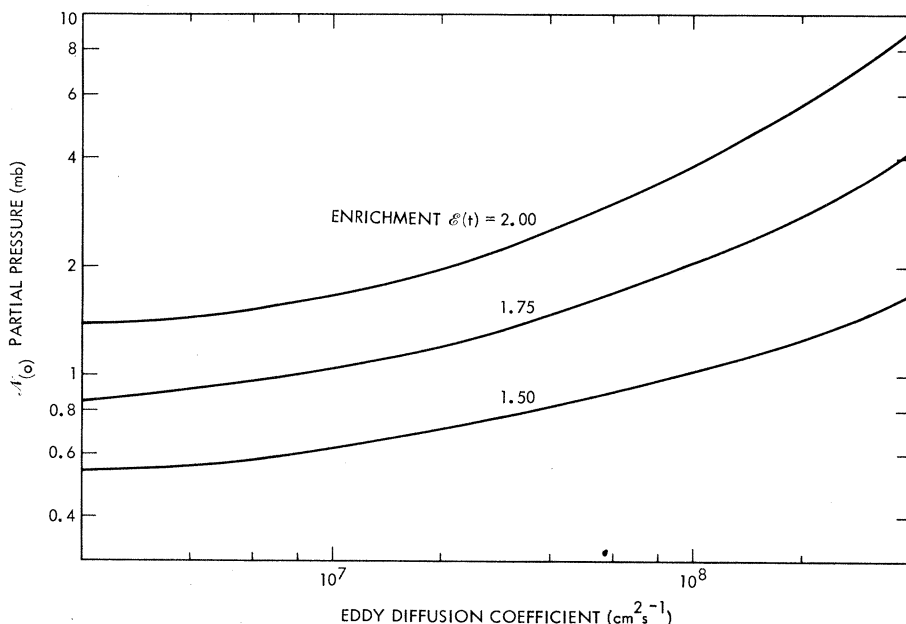


Fig. 2. Minimum initial abundances of N_2 required to supply enrichments of ^{15}N in the present atmosphere of magnitude 50, 75, and 100 percent, as functions of the value assumed for the eddy diffusion coefficient in the upper atmosphere. A diffusion coefficient of $10^8 \text{ cm}^2 \text{ sec}^{-1}$ would imply a turbopause located at an altitude of about 120 km.

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

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

and it may be readily shown that:

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

where $\mathcal{N}(0)$ denotes the initial abundance of N_2 , and $\mathcal{N}(t)$ 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 $\mathcal{E}(t)$ or, equivalently, it would imply a larger value for $\mathcal{N}(0)$ corresponding to any particular choice of $\mathcal{E}(t)$.

Values for $\mathcal{N}(0)$ are shown in Fig. 2, for several values of the enrichment factor $\mathcal{E}(t)$, 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 $10^8 \text{ cm}^2 \text{ sec}^{-1}$, 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.

ALFRED O. NIER

School of Physics and Astronomy,
University of Minnesota,
Minneapolis 55455

MICHAEL B. MCELROY

YUK LING YUNG

Center for Earth and Planetary Physics,
Harvard University,
Cambridge, Massachusetts 02138

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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.

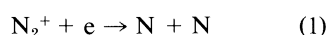
2 September 1976

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).

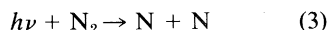
Escape of nitrogen from Mars may proceed by production of fast atoms in the exosphere, by either dissociative recombination of N_2^+ (3)



or electron impact dissociation of N_2 (4)



or predissociation of N_2 (5)



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 $400^\circ K$, 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).