OXYGEN ISOTOPES IN THE MARTIAN ATMOSPHERE: IMPLICATIONS FOR THE EVOLUTION OF VOLATILES

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Abstract—Non-thermal escape of oxygen by recombination of exospheric O$_2^+$ combined with diffusive separation of gases at lower altitude provides a mechanism through which the Martian atmosphere may be enriched in $^{18}$O relative to $^{16}$O. Measurement of the abundance of $^{18}$O relative to $^{16}$O together with a determination of the turbopause may be used to develop important constraints on the history of Martian volatiles. Models for the interpretation of these data are developed and discussed in light of present information.

1. INTRODUCTION

Recombination processes in the Martian ionosphere provide an important source of energetic oxygen atoms. The atoms are formed mainly by

\[ \text{O}_2^+ + e \rightarrow \text{O} + \text{O}, \quad (1) \]

with some contribution from

\[ \text{CO}_2^+ + e \rightarrow \text{CO} + \text{O}, \quad (2) \]

and one expects that a significant fraction of the atoms in (1) and (2) should escape the planet’s gravitational field if their velocity vectors are oriented in a proper direction (McElroy, 1972). The escape flux may be estimated with some precision. Its magnitude is related in a fairly straightforward manner to the rate for ionization of gas in the planetary exosphere.

An overwhelming number of all photoions formed in upper regions of the Martian atmosphere will react ultimately to form O$_2^+$ (McElroy and McConnell, 1971; Stewart, 1972), by reaction sequences such as

\[ h\nu + \text{CO}_2 \rightarrow \text{CO}_2^+ + e \quad (3) \]

followed by

\[ \text{CO}_2^+ + \text{O} \rightarrow \text{CO} + \text{O}_2^+, \quad (4) \]

or by

\[ h\nu + \text{O} \rightarrow \text{O}^+ + e \quad (5) \]

followed by

\[ \text{O}^+ + \text{CO}_2 \rightarrow \text{O}_2^+ + \text{CO}. \quad (6) \]

This conclusion holds even for minor products such as Ar$^+$, CO$^+$ or N$_2^+$, which are removed mainly by

\[ \text{Ar}^+ + \text{CO}_2 \rightarrow \text{Ar} + \text{CO}_2^+ \quad (7) \]

\[ \text{CO}^+ + \text{CO}_2 \rightarrow \text{CO} + \text{CO}_2^+ \quad (8) \]

and

\[ \text{N}_2^+ + \text{CO}_2 \rightarrow \text{N}_2 + \text{CO}_2^+ \quad (9) \]

followed by (4). For each photoion formed in the Martian exosphere two oxygen atoms will be released with energy sufficient to escape the planet’s gravitational field. One of these atoms will have its initial velocity vector oriented in the upward hemisphere and may escape therefore without undergoing further collision. The escape rate, set mainly by atomic processes (collision cross sections and cross sections for photoionization), and by the magnitude of the flux of incident solar radiation, may be estimated to have an average value equal to about $6 \times 10^7$ atoms/cm$^2$/sec (McElroy, 1972). This result should be accurate to within about a factor of 2.

Non-thermal escape, by the mechanism outlined above, has a number of important consequences for Mars. McElroy and Donahue (1972) argued that escape of oxygen could regulate the bulk chemistry of the lower atmosphere (see, also, Liu and Donahue, 1976), that it would serve to control the formation and removal of both O$_2$ and CO, in such a manner as to ensure an escape flux for H equal to exactly twice that for O. Escape of H is supplied mainly by upward transport of H$_2$, which may be decomposed in the thermosphere (McElroy and Hunten, 1969) by

\[ \text{CO}_2^+ + \text{H}_2 \rightarrow \text{CO}_2\text{H}^+ + \text{H} \quad (10) \]
followed by
\[ \text{CO}_2\text{H}^+ + e \rightarrow \text{CO}_2 + \text{H}, \]  
(11)
and by
\[ \text{O}(^1\text{D}) + \text{H}_2 \rightarrow \text{OH} + \text{H}. \]  
(12)
Molecular hydrogen is formed in the lower atmosphere, by
\[ \text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2, \]  
(13)
and the production rate for the gas is a fairly sensitive function of the concentration assumed for \( \text{O}_2 \) (McElroy, 1973). Molecular oxygen is formed mainly by
\[ \text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H} \]  
(14)
and removed either by
\[ h\nu + \text{O}_2 \rightarrow \text{O} + \text{O} \]  
(15)
followed by
\[ \text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2 \]  
(16)
and
\[ \text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}, \]  
(17)
or by
\[ \text{H} + \text{O}_2 + \text{CO}_2 \rightarrow \text{HO}_2 + \text{CO}_2 \]  
(18)
followed by
\[ \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2, \]  
(19)
\[ h\nu + \text{H}_2\text{O}_2 \rightarrow 2\text{OH}, \]  
(20)
and (17). Reaction (17) represents the dominant path for removal of CO.

This paper focuses on another possible consequence of oxygen escape. We expect that diffusive separation in the upper atmosphere should lead to a small enrichment in the exospheric concentration of \(^{16}\text{O}\) with respect to \(^{18}\text{O}\). The escape rate for the lighter isotope will be enhanced accordingly and one might anticipate that the volatile elements of the Martian atmosphere and regolith should be enriched to some extent in \(^{18}\text{O}\). The degree of enrichment depends on a number of factors: the extent to which diffusive separation may proceed in the upper atmosphere; the detailed history for the evolution of volatiles, whether volatiles were released at an early stage in planetary evolution or at a slow steady rate over geologic time; the available source of volatiles; and the rate at which oxygen isotopes may be exchanged between different compartments of the total volatile reservoir. We shall approach the problem here from a purposely simple perspective. We consider first the case for which the effective reservoir of active volatiles is taken to be relatively small, comparable in size to the total amount of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) now present in the atmosphere. The atmosphere may lose H and O either to space or to the surface, where these elements may be immobilized by incorporation in surface rocks (Huguenin, 1973a, 1973b, 1974, 1976; McElroy and Kong, 1976). We shall assume that the release of \( \text{H}_2\text{O} \) from the crust is precisely that required to balance loss of the constituent atoms to space and to the ground. Section 3 explores a more realistic model, in which atmospheric oxygen may be exchanged with a relatively large reservoir of oxygen, present for example as \( \text{CO}_2 \) ice in the polar cap, or as available \( \text{H}_2\text{O} \) in the deep regolith. We shall attempt to isolate factors which might lead to a net change in the relative concentrations of \(^{16}\text{O}\) and \(^{18}\text{O}\). As we shall see, the isotopic composition of the atmosphere may be expected to depend in a fairly sensitive fashion on the degree to which mass mixing may proceed in the upper atmosphere, and it should be influenced also to an appreciable extent by exchange of atmospheric oxygen with surface and subsurface volatiles. The Viking spacecraft scheduled to land on Mars on 4 July 1976, should provide a direct indication of the strength for vertical mixing in the thermosphere. Viking should also provide a direct measurement for the abundance of \(^{18}\text{O}\) relative to \(^{16}\text{O}\). It should be possible on this basis to develop a number of important constraints with regard to the evolutionary history of volatiles on Mars. This paper is intended to provide a framework within which this new information may be assessed and assimilated. It is clear in any event that the degree to which the present atmosphere is enriched in \(^{18}\text{O}\) must be relatively small, less than about 10% (Young, 1971). Mixing processes in the upper atmosphere must be extraordinarily vigorous. Alternatively atmospheric oxygen must exchange readily with a rather large store of surface and subsurface volatiles on a time scale of about \( 10^9 \) years. The real situation may involve some combination of these extremes.

2. ISOTOPIC COMPOSITION: THE LIMITING CASE FOR A VANISHING EXCHANGE WITH THE SUBSURFACE RESERVOIR

Let \( \phi_1 \) denote the magnitude of the rate at which oxygen atoms escape to space (cm\(^{-2}\)/sec), and let \( \phi_2 \) represent the rate at which oxygen atoms may be immobilized by heterogeneous processes at the surface. We shall assume here that water is released from the surface at a rate \( \phi_3 \), such that
\[ \phi_3 = \phi_1 + \phi_2. \]  
(21)
Let \( a_0 \) denote the total number of oxygen atoms (cm\(^{-2}\)) present in the atmosphere as \( \text{CO}_2 \), \( 4.0 \times 10^{23} \) if we assume a mean surface pressure of 6 mbars. Let \( b_0 \) represent the number of oxygen atoms present as \( \text{H}_2\text{O} \), about \( 1.9 \times 10^{20} \) if we use Barker's
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(1976) value for the concentration of the gas in relatively moist regions of the atmosphere, about 50 precipitable microns.

It is convenient to introduce a further parameter, \( R \), which defines the extent to which the exosphere may be depleted in \(^{18}\text{O}\) due to diffusive separation at lower altitudes:

\[
R = \frac{f_c}{f_0}.
\]

(22)

Here \( f_c \) denotes the abundance of \(^{18}\text{O}\) relative to \(^{16}\text{O}\) at the critical level and \( f_0 \) is the analogous quantity for the bulk atmosphere. The deficiency parameter \( R \) may be readily derived as a function of the eddy diffusion coefficient \( K \) taken to model the effects of mixing near the turbopause. Values for \( R \) as a function of \( K \) are shown in Fig. 1.

We suppose that the abundance of \(^{18}\text{O}\) relative to \(^{16}\text{O}\) is given by \( f_0(0) \) at some initial time \( t = 0 \). The abundance at subsequent time \( t \) is given by:

\[
f_0(t) = f_0(0) \left\{ \frac{\phi_1 + \phi_2 - (1 - R)\phi_1 \times \exp[-(R\phi_1 + \phi_2)/(a_0 + b_0)t]}{R\phi_1 + \phi_2} \right\}.
\]

(23)

It is clear that the atmosphere should become enriched in \(^{18}\text{O}\). The enrichment should occur on a time scale \( \tau \) given by

\[
\tau = \frac{a_0 + b_0}{R\phi_1 + \phi_2}
\]

(24)

and we may obtain an upper bound to \( \tau \) if we take \( \phi_2 \) equal to zero, i.e. if we ignore the possible sink

for oxygen at the surface. With \( \phi_1 \) set equal to \( 6 \times 10^7 \), the value appropriate for non-thermal escape, and with values for \( a_0 \) and \( b_0 \) discussed above, \( \tau \) is given by:

\[
\tau_{\text{max}} = 2 \times 10^8 \, R^{-1} \, \text{yr}.
\]

(25)

The u.v. spectrometer on Mariners 6 and 7 (Barth et al., 1969, 1971, 1972) indicated that atomic oxygen should be a minor constituent of the Martian thermosphere (see, also, Stewart, 1972 and Strickland et al., 1972). In order to account for these data, one requires an eddy diffusion coefficient of order \( 5 \times 10^8 \, \text{cm}^2/\text{sec} \) (McElroy and McConnell, 1971). This choice for \( K \) implies a value for \( R \) equal to about 0.8 (see Fig. 1) and an upper limit for \( \tau \) of magnitude \( 2.5 \times 10^8 \, \text{yr} \). For times longer than \( 2.5 \times 10^8 \, \text{yr} \), \( f_0(t) \) approaches an asymptotic value given by

\[
f_0(t) = f_0(0) \left\{ \frac{\phi_1 + \phi_2}{R\phi_1 + \phi_2} \right\}.
\]

(26)

With \( \phi_2 = 0 \) and \( R = 0.8 \), we expect an enrichment for atmospheric \(^{18}\text{O}\) of order 20%, a value which exceeds the upper limit imposed by ground based spectroscopy (Young, 1971), about 10%. An enrichment of 10%, with \( \phi_2 = 0 \), would require an eddy coefficient \( K \) of order \( 4 \times 10^9 \, \text{cm}^2/\text{sec} \), and this result should apply on a time scale of almost \( 2 \times 10^8 \, \text{yr} \).

It is difficult to obtain a quantitative estimate for \( \phi_2 \). Huguenin (1973a, 1973b, 1974, 1976) proposed a mechanism which could provide an important sink for oxygen at the surface. He noted that dark areas on Mars appear to contain abundant sources of Fe\(^{2+}\) minerals, present as pyroxene, olivine and magnetite. Oxidation of ferrosilicates could occur, mediated by adsorption of \( \text{H}_2\text{O} \) on surface layers. The bulk reaction may be written in the form (McElroy and Kong, 1976)

\[
\text{hv} + 2\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{FeOOH} + 4\text{H}^+.
\]

(27)

Protons would diffuse to the interior, replacing Fe\(^{3+}\) in such a manner as to conserve charge neutrality. Oxidation of magnetite could proceed by:

\[
\text{hv} + 2\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{O}_2 \rightarrow 3\text{Fe}_2\text{O}_3,
\]

(28)

if we denote the magnitude of the rate for adsorption of oxygen by \( \phi_2 \) as before, and the rate for adsorption of H by \( \phi_{\text{H}_2} \), it would seem clear that the associated fluxes should satisfy the relation \( \phi_2 > 0.5 \phi_{\text{H}_2} \). The sink for O, over and above that supplied by \( \text{H}_2\text{O} \), may be written as

\[
\phi_2^* = \phi_2 - \frac{1}{2}\phi_{\text{H}_2}.
\]

(29)
and an atmospheric analysis may be used to place an important limit on $\phi_2^*$. McElroy and Kong (1976) argued that $\phi_2^*$ could not exceed $3.3 \times 10^7$ atoms/cm/sec. If (27) were to represent the dominant path for oxidation of surface rocks, $\phi_2$ could be as large as $1.3 \times 10^8$ atoms/cm$^2$/sec.

Formation of CaCO$_3$ offers an additional possible sink for oxygen. The bulk reaction here may be written either as

$$\text{CaSiO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{H}_2\text{SiO}_3 + \text{CaCO}_3, \tag{30}$$

or as

$$\text{CaSiO}_3 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{SiO}_3 + \text{CaCO}_3, \tag{31}$$

where CaSiO$_3$ represents a suitable source for mineral calcium. Reactions (30) and (31) involve no net change in the oxidation state of Ca. Oxygen should be removed therefore in such a manner as to ensure a stoichiometric balance in the values for $\phi_2$ and $\phi_{H_2}$, i.e. $\phi_2 = \frac{1}{2}\phi_{H_2}$. The atmospheric analysis described by McElroy and Kong (1976) cannot be used therefore in this case to delimit the possible range of values for $\phi_2$. On the other-hand, there is no direct information to support an important role for either (30) or (31) on Mars. Both reactions involve a sink not only for oxygen but also for carbon. The analysis described above was predicated on the assumption that the carbon content of the volatile reservoir should remain fixed in time. Modifications required in order to account for possible time variability in volatile carbon are discussed in Section 3.

Huguenin (1976) quotes a large range of values for formation of Fe$_2$O$_3$ on Mars, between $10^{-4}$ \mu m/yr and $10^{-1}$ \mu m/yr. The corresponding sink for oxygen, $\phi_2$, would lie between $6 \times 10^6$ and $6 \times 10^7$ atoms/cm$^2$/sec, and we may note that the limit derived by McElroy and Kong (1976) is consistent with this analysis. Enrichment factors for $^{18}$O, $f_{0}(t)/f_{0}(0)$, for several values of $\phi_2$, are shown in Fig. 2 with $K$ set equal to $5 \times 10^8$ cm$^2$/sec. The enrichment factor would be exceedingly large if the eddy diffusion coefficient had a value similar to that on the Earth (Colegrove et al., 1966), about $10^6$ cm$^2$/sec, as many be seen from Fig. 3. Asymptotic values for $f_{0}(t)/f_{0}(0)$ are shown in Fig. 4, with a range of values for $K$ and $\phi_2$.

It may be of interest to consider the rate at which isotopically labeled oxygen is exchanged between different compartments of the atmospheric reservoir. Consider an oxygen atom released at time $t = 0$ as a component of H$_2$O. The atom may be transferred to CO$_2$ by

$$h \nu + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H} \tag{32}$$

or by

$$\text{O}^{(1D)} + \text{H}_2\text{O} \rightarrow 2\text{OH} \tag{33}$$

followed by (17). It may be transferred to O$_2$ by (14), or by

$$h \nu + \text{CO}_2 \rightarrow \text{CO} + \text{O} \tag{34}$$

followed by (14). It may be used to make CO, by (34), or O$_3$, by

$$\text{O} + \text{O}_2 + \text{CO}_2 \rightarrow \text{O}_3 + \text{CO}_2, \tag{35}$$

Fig. 2. Enrichment factor for $^{18}$O, $f_{0}(t)/f_{0}(0)$, as a function of time for $\phi_2 = 0$, $3.3 \times 10^7$ and $1.3 \times 10^8$ atoms/cm$^2$/sec, respectively. The eddy diffusion coefficient $K$ is set equal to $5 \times 10^8$ cm$^2$/sec.

Fig. 3. Same as for Fig. 2, with $K$ equal to $1 \times 10^6$ cm$^2$/sec.
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and is removed ultimately by escape or by (27–32). With present models for the atmospheric chemistry (McElroy and Donahue, 1972; Kong, 1976), the atom will spend a total time of order $1.2 \times 10^4$ yr in the atmosphere, mostly as CO$_2$. Approximately $3 \times 10^7$ yr will be spent as H$_2$O, and the residence times for O$_2$, CO, O$_3$ and O are $1 \times 10^6$ yr, $5 \times 10^4$ yr, $1 \times 10^5$ yr and 10 yr respectively.

3. ISOTOPIC COMPOSITION: THE INFLUENCE OF A SIGNIFICANT SUBSURFACE RESERVOIR

We assumed in Section 2 that atmospheric CO$_2$ should represent the major reservoir for volatile oxygen. The reservoir was supplied by photodecomposition of H$_2$O, released from the surface at precisely the rate required to balance escape plus surface immobilization. The total reservoir size, $a_0 + b_0$, remained constant with time, and we did not explicitly consider the influence of exchange between atmospheric and subsurface oxygen. Limitations imposed by this assumption are relaxed here. We consider an initial source of oxygen, as CO$_2$, with magnitude $a$, of which an amount $a_0$ is taken to be present in the atmosphere. The analogous quantities for H$_2$O are $b(t)$ and $b_0$.

The time evolution of atmospheric $^{18}$O is given now by:

$$f_0(t) = f_0(0) \left[ \frac{a + b(0)}{a + b(t)} \right]^{(1-R)/\phi_1(\phi_1 + \phi_2)}$$

(36)

It may be readily shown that (36) will reduce to (23) if we consider the limit for which $(\phi_1 + \phi_2)t < b(0)$, with $a$ equal to $a_0$ and $b(0)$ equal to $b_0$. The subsurface reservoir will play an important role for $t$ of order $a + b(0)/(\phi_1 + \phi_2)$. Figure 5 shows enrichment factors $f_0(t)/f_0(0)$ with $t$ equal to the age of the planet, about $5 \times 10^9$ yr. Results are given as a function of the value assumed for the eddy diffusion coefficient $K$ and for the initial size of the total oxygen reservoir, $a + b(0)$. The right hand axes give the corresponding quantities of CO$_2$ and H$_2$O which would apply if these compounds were individually to constitute the major source for volatile oxygen. Figures 5 describes the case $\phi_2 = 0$. Results
with $\phi_1 = 3.3 \times 10^7$, $1.3 \times 10^8$ and $10^9$ are shown in Fig. 6, with an enrichment factor, $f_0(t)/f_0(0)$, set equal to 1.05, somewhat below the present upper limit of 1.10 (Young, 1971). The results in Figs. 5 and 6 are based on the assumption that the volatiles were released $5 \times 10^9$ yr ago. Figures 7 and 8 summarize the behavior expected if Mars should have acquired its volatiles relatively recently, about $1 \times 10^9$ yr ago.

Consider a representative case, with $K$ equal to $5 \times 10^8$ cm$^2$/sec, a value derived by McElroy and McConnell (1971), with $\phi_2$ equal to $1 \times 10^8$ cm$^{-2}$/sec, the upper limit set by McElroy and Kong (1976) for oxidation of iron, and with an enrichment factor, $f_0(t)/f_0(0)$, equal to 1.05. As may be seen from Fig. 6, this situation could arise if the Martian atmosphere were to exchange its assumed oxygen content with a surface or subsurface reservoir of CO$_2$ or H$_2$O of order 1 bar. Fanale and Cannon (1974) (see also, Fanale, 1976) estimate an average concentration of CO$_2$ in the Martian regolith of magnitude $0.4 \text{ g/cm}^2$. The corresponding value for H$_2$O is about $1 \text{ g/cm}^2$. An effective reservoir of 1 bar would require active exchange between the atmosphere and regolith to a depth of about 1 km. One might expect significant exchange of CO$_2$ and H$_2$O to proceed to this depth if the effective insolation at Mars should vary on a time scale of order $10^6$ yr (Fanale and Cannon, 1974). Variations in insolation on a time scale of $1.2 \times 10^5$ yr would occur due to change in the obliquity of the planet, as discussed by Ward (1973), and there may be variations in insolation on a longer time scale due to change in solar luminosity (Sagan et al., 1973). The time required for diffusive exchange of H$_2$O between the surface and a depth of 1 km would be about $3 \times 10^6$ yr if the diffusion coefficient had a value of order $10^{-4}$ cm$^2$/sec.

Equations (36) and (37) may be readily amended to allow for the possible effect of reactions (30) and (31). If $\psi$ represents the rate (molecules/cm$^2$/sec) for removal of CO$_2$, then

$\frac{f_0(t)}{f_0(0)} = \left[ \frac{a(t) + b(t)}{a(0) + b(0)} \right]^{(1-R)/4(2+4)}$

with

$a(t) = a(0) - 2\psi t$

and

$b(t) = b(0) - (\phi_1 + \phi_2)t - \psi t$.

The possible influence of (30) and (31) may be described therefore by a suitable choice of values for $\phi_2$ in (36) and (37).

We assumed here that the regolith acquired its total volatile content of oxygen at time $t = 0$. Suppose that degassing from the mantle were to take place at a slow steady rate over geologic time. Let $S_1$ and $S_2$ denote degassing rates for CO$_2$ and H$_2$O respectively. The analysis may be readily modified to allow for this possibility. We find

$f_0(t) = f_0(0) \left( \frac{S_1 + S_2 - \lambda(1-R)\phi_1}{S_1 + S_2 - \phi_1(1-R)} \right)$

with

$\lambda = \left( \frac{A}{A + [S_1 + S_2 - (\phi_1 + \phi_2)t]} \right) ^{S_1 + S_2 - \phi_1(1-R)}$.

Here $A$ denotes the initial source of oxygen in the combined atmosphere-regolith reservoir: (38) reduces to (36) in the limit $(S_1 + S_2) \to 0$. Results are shown in Fig. 9, with a particular choice of values for $A$, $\phi_2$ and $t$. 

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**Figure 7.** Same as Fig. 5, with $t = 1 \times 10^9$ yr.

**Figure 8.** Same as Fig. 6, with $t = 1 \times 10^9$ yr.
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Fig. 9. Enrichment factors as a function of eddy diffusion coefficient $K$, and the total amount of outgassed volatiles $(S_1 + S_2)t$, with $A = 0$, $\phi_2 = 0$ and $t = 5 \times 10^9$ yr.

4. CONCLUDING REMARKS

A precise measurement of the isotopic composition of the Martian atmosphere, coupled with an accurate determination for the location of the turbopause, may be used to impose a variety of constraints on the evolution of volatiles for Mars. It is hoped that Viking may provide an opportunity to exploit the analysis presented here. Viking may contribute also in limiting the range of uncertainty on $\phi_2$. Information on the time evolution of Martian volatiles should, in addition, enhance our understanding of processes which occurred on the early Earth.

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NOTE ADDED IN PROOF

Viking landed successfully on the surface of Mars on 20 July 1976. A preliminary report of results from the various investigations has appeared already, in Science 193, No. 4255, 27 August 1976. Further information is presented in Science 194, No. 4260, 1 October 1976. The isotopic abundance ratios $^{13}C$ and $^{18}O$ for the Martian atmosphere are similar to Earth, consistent with the discussion given here. The Martian atmosphere is appreciably enriched in $^{15}N$ relative to $^{14}N$, by about 80%, and the methodology developed in this paper was applied by Nier et al. (Science 194, 68, 1976) and McElroy et al. (Science 194, 70, 1976) to place important constraints on the past evolutionary history of Mars.