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

MICHAEL B. MCELROY
and
**YUK LING YUNG**
Center for Earth and Planetary Physics, Harvard University, Cambridge, MA 02138, U.S.A.

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
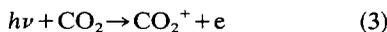
$$O_2^+ + e \rightarrow O + O, \tag{1}$$
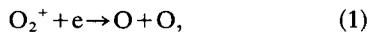
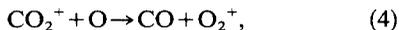with some contribution from

$$CO_2^+ + e \rightarrow CO + O, \tag{2}$$
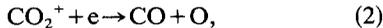
and one expects that a significant fraction of the atoms in (1) and (2) should escape the planet's gravitional field if their velocity vectors are oriented in a proper direction (McElroy, 1972). The escape flux may be estimated with some precision. Its magnitude is related in a fairly straightforward 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
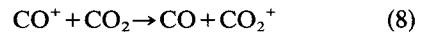
$$h\nu + CO_2 \rightarrow CO_2^+ + e \tag{3}$$

followed by

$$CO_2^+ + O \rightarrow CO + O_2^+, \tag{4}$$

or by

$$h\nu + O \rightarrow O^+ + e \tag{5}$$

followed by

$$O^+ + CO_2 \rightarrow O_2^+ + CO. \tag{6}$$

This conclusion holds even for minor products such as Ar^+, CO^+ or N_2^+, which are removed mainly by

$$Ar^+ + CO_2 \rightarrow Ar + CO_2^+ \tag{7}$$

$$CO^+ + CO_2 \rightarrow CO + CO_2^+ \tag{8}$$

and

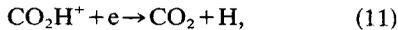$$N_2^+ + CO_2 \rightarrow N_2 + CO_2^+ \tag{9}$$

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 6×10^7 atoms/cm²/sec (McElroy, 1972). This result should be accurate to within about a factor of 2.
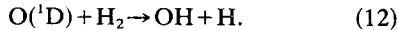
Non-thermal escape, by the mechanism outlined above, has a number of important consequences for Mars. McElroy and Donahue (1972) argued that escape of oxygen could regulate the bulk chemistry of the lower atmosphere (see, also, Liu and Donahue, 1976), that it would serve to control the formation and 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
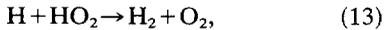
$$CO_2^+ + H_2 \rightarrow CO_2H^+ + H \tag{10}$$

1

followed by

$$CO_2H^+ + e \rightarrow CO_2 + H, \qquad (11)$$

and by

$$O(^1D) + H_2 \rightarrow OH + H. \qquad (12)$$

Molecular hydrogen is formed in the lower atmosphere, by
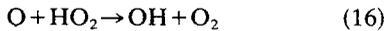
$$H + HO_2 \rightarrow H_2 + O_2, \qquad (13)$$

and the production rate for the gas is a fairly sensitive function of the concentration assumed for O_2 (McElroy, 1973). Molecular oxygen is formed mainly by
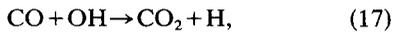
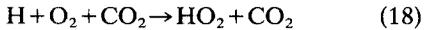$$O + OH \rightarrow O_2 + H \qquad (14)$$

and removed either by

$$h\nu + O_2 \rightarrow O + O \qquad (15)$$

followed by

$$O + HO_2 \rightarrow OH + O_2 \qquad (16)$$

and

$$CO + OH \rightarrow CO_2 + H, \qquad (17)$$

or by

$$H + O_2 + CO_2 \rightarrow HO_2 + CO_2 \qquad (18)$$

followed by

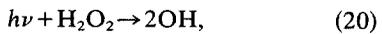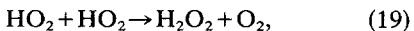$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2, \qquad (19)$$

$$h\nu + H_2O_2 \rightarrow 2OH, \qquad (20)$$

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}O with respect to ^{18}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}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 voltile 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 CO_2 and H_2O 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 H_2O 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 CO_2 ice in the polar cap, or as available H_2O in the deep regolith. We shall attempt to isolate factors which might lead to a net change in the relative concentrations of ^{16}O and ^{18}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}O relative to ^{16}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}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 ϕ_1 denote the magnitude of the rate at which oxygen atoms escape to space (cm^{-2}/sec), and let ϕ_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 ϕ_3 such that

$$\phi_3 = \phi_1 + \phi_2. \qquad (21)$$

Let a_0 denote the total number of oxygen atoms (cm^{-2}) present in the atmosphere as CO_2, 4.0×10^{23} if we assume a mean surface pressure of 6 mbars. Let b_0 represent the number of oxygen atoms present as H_2O, about 1.9×10^{20} if we use Barker's

(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}O due to diffusive separation at lower altitudes:

$$R = \frac{f_c}{f_0}. \tag{22}$$

Here f_c denotes the abundance of ^{18}O relative to ^{16}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}O relative to ^{16}O is given by $f_0(0)$ at some initial time $t = 0$. The abundance at subsequent time t is given by:

$$f_0(t) = f_0(0) \left\{ \frac{\phi_1 + \phi_2 - (1-R)\phi_1 \times \exp\left[-(R\phi_1 + \phi_2)/(a_0+b_0)]t\right)}{R\phi_1 + \phi_2} \right\}. \tag{23}$$

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

$$\tau = \frac{a_0 + b_0}{R\phi_1 + \phi_2} \tag{24}$$

and we may obtain an upper bound to τ if we take ϕ_2 equal to zero, i.e. if we ignore the possible sink
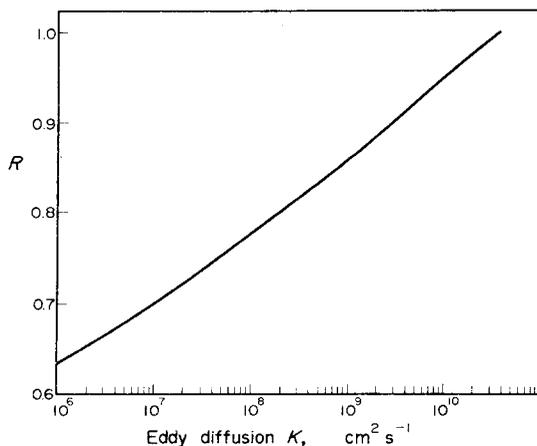
FIG. 1. VALUES OF R, THE DEFICIENCY PARAMETER FOR ^{18}O IN THE EXOSPHERE, AS A FUNCTION OF THE EDDY DIFFUSION COEFFICIENT K.

for oxygen at the surface. With ϕ_1 set equal to 6×10^7, the value appropriate for non-thermal escape, and with values for a_0 and b_0 discussed above, τ is given by:

$$\tau_{max} = 2 \times 10^8 \, R^{-1} \, yr. \tag{25}$$

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 $5 \times 10^8 \, cm^2/sec$ (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 τ of magnitude $2.5 \times 10^8 \, yr$. For times longer than $2.5 \times 10^8 \, yr$, $f_0(t)$ approaches an asymptotic value given by

$$f_0(t) = f_0(0) \left\{ \frac{\phi_1 + \phi_2}{R\phi_1 + \phi_2} \right\}. \tag{26}$$

With $\phi_2 = 0$ and $R = 0.8$, we expect an enrichment for atmospheric ^{18}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 $4 \times 10^9 \, cm^2/sec$, and this result should apply on a time scale of almost $2 \times 10^8 \, yr$.

It is difficult to obtain a quantitative estimate for ϕ_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 H_2O on surface layers. The bulk reaction may be written in the form (McElroy and Kong, 1976)

$$h\nu + 2Fe^{2+} + \tfrac{1}{2}O_2 + 3H_2O \rightarrow 2FeOOH + 4H^+. \tag{27}$$
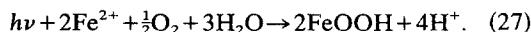
Protons would diffuse to the interior, replacing Fe^{2+} in such a manner as to conserve charge neutrality. Oxidation of magnetite could proceed by:
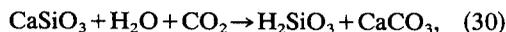
$$h\nu + 2Fe_3O_4 + \tfrac{1}{2}O_2 \rightarrow 3Fe_2O_3, \tag{28}$$
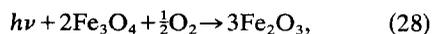
if we denote the magnitude of the rate for adsorption of oxygen by ϕ_2 as before, and the rate for adsorption of H by ϕ_H, it would seem clear that the associated fluxes should satisfy the relation $\phi_2 > 0.5 \phi_H$. The sink for O, over and above that supplied by H_2O, may be written as
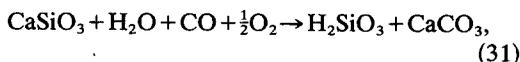
$$\phi_2^* = \phi_2 - \tfrac{1}{2}\phi_H, \tag{29}$$

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 3.3×10^7 atoms/cm/sec. If (27) were to represent the dominant path for oxidation of surface rocks, ϕ_2 could be as large as 1.3×10^8 atoms/cm^2/sec.

Formation of $CaCO_3$ offers an additional possible sink for oxygen. The bulk reaction here may be written either as

$$CaSiO_3 + H_2O + CO_2 \rightarrow H_2SiO_3 + CaCO_3, \quad (30)$$

or as

$$CaSiO_3 + H_2O + CO + \tfrac{1}{2}O_2 \rightarrow H_2SiO_3 + CaCO_3, \quad (31)$$

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 ϕ_2 and ϕ_H, i.e. $\phi_2 = \tfrac{1}{2}\phi_H$. The atmospheric analysis described by McElroy and Kong (1976) cannot be used therefore in this case to delimit the possible range of values for ϕ_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_2O_3 on Mars, between $10^{-4}\ \mu$m/yr and $10^{-1}\ \mu$m/yr. The corresponding sink for oxygen, ϕ_2, would lie between 6×10^6 and 6×10^9 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 ϕ_2, are shown in Fig. 2 with K set equal to 5×10^8 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 ϕ_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_2O. The atom may be
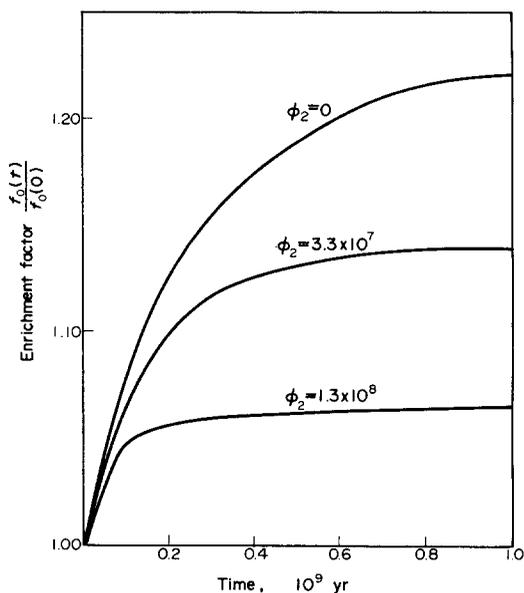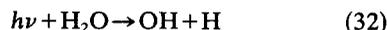

FIG. 2. ENRICHMENT FACTOR FOR ^{18}O, $f_0(t)/f_0(O)$, AS A FUNCTION OF TIME FOR $\phi_2 = 0$, 3.3×10^7 AND 1.3×10^8 atoms/cm^2/sec, RESPECTIVELY. THE EDDY DIFFUSION COEFFICIENT K IS SET EQUAL TO 5×10^8 cm^2/sec.

transferred to CO_2 by

$$h\nu + H_2O \rightarrow OH + H \quad (32)$$

or by

$$O(^1D) + H_2O \rightarrow 2OH \quad (33)$$

followed by (17). It may be transferred to O_2 by (14), or by

$$h\nu + CO_2 \rightarrow CO + O \quad (34)$$
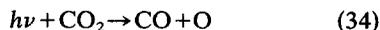
followed by (14). It may be used to make CO, by (34), or O_3, by

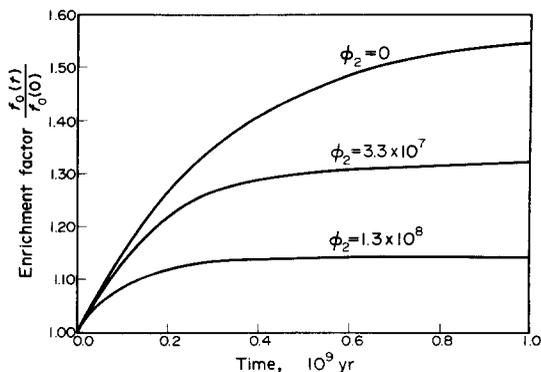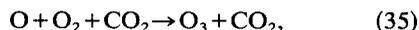$$O + O_2 + CO_2 \rightarrow O_3 + CO_2, \quad (35)$$

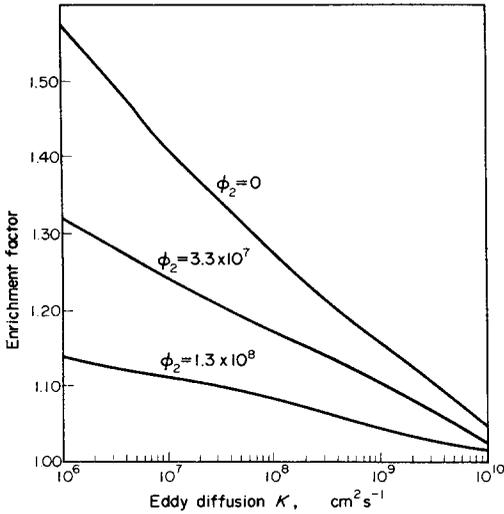FIG. 3. SAME AS FOR FIG. 2, WITH K EQUAL TO 1×10^6 cm^2/sec.

FIG. 4. ASYMPTOTIC VALUES FOR THE ENRICHMENT FACTOR, $f_0(t)/f_0(0)$, AS A FUNCTION OF THE EDDY DIFFUSION CO-EFFICIENT K, FOR $\phi_2 = 0$, 3.3×10^7 AND 1.3×10^8 cm^{-2}/sec RESPECTIVELY.

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 1.2×10^8 yr in the atmosphere, mostly as CO_2. Approximately 3×10^7 yr will be spent as H_2O, and the residence times for O_2, CO, O_3 and O are 1×10^6 yr, 5×10^4 yr, 1×10^5 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 photo-decomposition of H_2O, 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_2O are $b(t)$ and b_0.

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

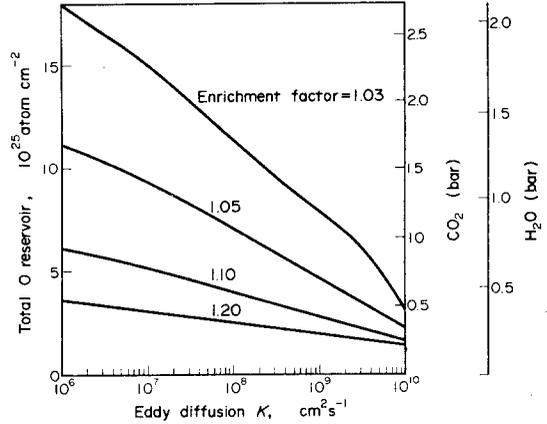$$f_0(t) = f_0(0) \left[\frac{a + b(0)}{a + b(t)} \right]^{(1-R)\phi_1/(\phi_1+\phi_2)}$$

(36)

FIG. 5. ENRICHMENT FACTOR, $f_0(t)/f_0(0)$, FOR t EQUAL TO 5×10^9 yr AS A FUNCTION FOR THE EDDY DIFFUSION CO-EFFICIENT K AND THE INITIAL TOTAL OXYGEN RESERVOIR, $a + b(0)$, WITH $\phi_2 = 0$.

with

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

(37)

It may be readily shown that (36) will reduce to (23) if we consider the limit for which $(\phi_1 + \phi_2)t \ll b(0)$, 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 5×10^9 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_2O 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
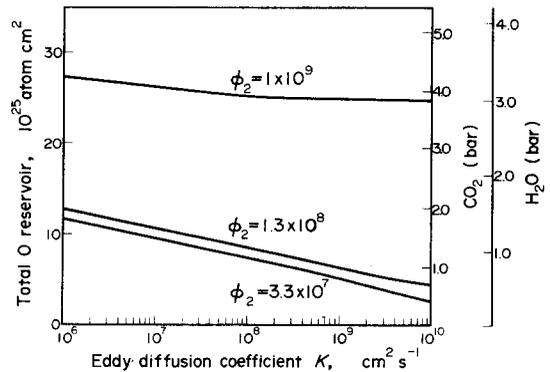

FIG 6. INITIAL TOTAL OXYGEN RESERVOIR AS A FUNCTION OF EDDY DIFFUSION COEFFICIENT K FOR AN ENRICHMENT FACTOR OF 1.05 AND $\phi_2 = 3.3 \times 10^7$, 1.3×10^8 AND 1×10^9 cm^{-2}/sec.

with $\phi_2 = 3.3 \times 10^7$, 1.3×10^8 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 5×10^9 yr ago. Figures 7 and 8 summarize the behavior expected if Mars should have acquired its volatiles relatively recently, about 1×10^9 yr ago.

Consider a representative case, with K equal to 5×10^8 cm^2/sec, a value derived by McElroy and McConnell (1971), with ϕ_2 equal to 1×10^8 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_2O 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 g/cm^2/m. The corresponding value for H_2O is about 1 g/cm^2/m. 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_2O 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 1.2×10^5 yr would occur due to change in the obliquity of the planet, as dicussed 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_2O between the surface and a depth
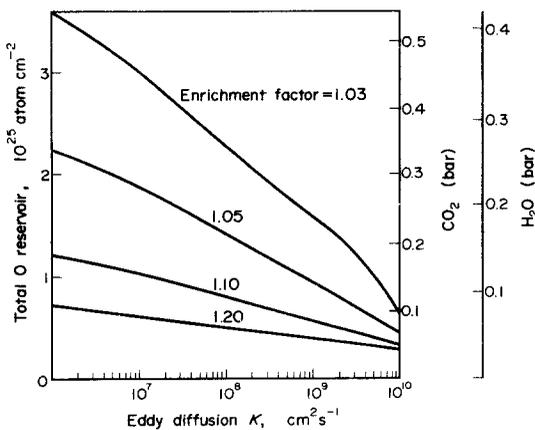

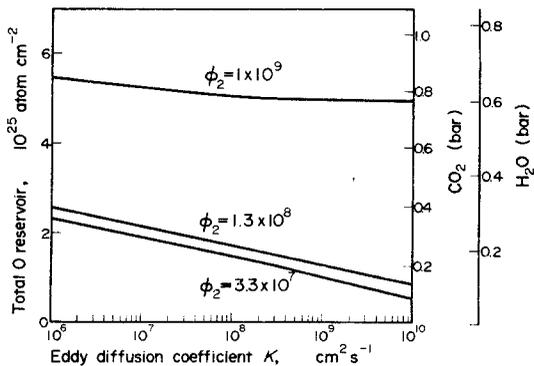FIG. 7. SAME AS FIG. 5, WITH $t = 1 \times 10^9$ yr.

FIG. 8. SAME AS FIG. 6, WITH $t = 1 \times 10^9$ yr.

of 1 km would be about 3×10^6 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 ψ represents the rate (molecules/cm^2/sec) for removal of CO_2, then

$$\frac{f_0(t)}{f_0(0)} = \left[\frac{a(0) + b(0)}{a(t) + b(t)} \right]^{(1-R)\phi_1/(\phi_1 + \phi_2 + 3\psi)}$$

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 ϕ_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_2O respectively. The analysis may be readily modified to allow for this possibility. We find

$$f_0(t) = f_0(0) \left\{ \frac{S_1 + S_2 - \lambda(1 - R)\phi_1}{S_1 + S_2 - \phi_1(1 - R)} \right\}. \tag{38}$$

with

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

$$\tag{39}$$

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, ϕ_2 and t.
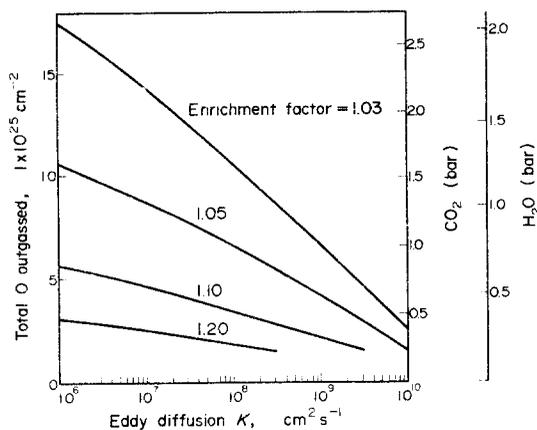
FIG. 9. ENRICHMENT FACTORS AS A FUNCTION OF EDDY DIFFUSION COEFFICIENT K, AND THE TOTAL AMOUNT OF OUTGASSED VOLATILES $(S_1 + S_2)t$, WITH $A = 0$, $\phi_2 = 0$ AND $t = 5 \times 10^9$ yr.

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 ϕ_2. Information on the time evolution of Martian volatiles should, in addition, enhance our understanding of processes which occurred on the early Earth.

REFERENCES

Barker, E. S. (1976). *Icarus* **28**, 247.
Barth, C. A., Pearce, J. B., Kelly, K. K., Wallace, L. and Fastie, W. G. (1967). *Science* **158**, 1675.
Barth, C. A., Fastie, W. G., Hord, C. W., Pearce, J. B., Kelly, K. K., Stewart, A. I., Thomas, G. E., Anderson, G. P. and Raper, O. E. (1969). *Science* **165**, 1004.
Barth, C. A., Hord, C. W., Pearce, J. B., Kelly, K. K., Anderson, G. P. and Stewart, A. I. (1971). *J. geophys. Res.* **76**, 2213.
Barth, C. A., Hord, C. W., Stewart, A. I. and Lane, A. L. (1972). *Science* **175**, 309.
Colegrove, F. D., Johnson, F. S. and Hanson, W. B. (1966). *J. geophys. Res.* **71**, 2227.
Fanale, F. P. (1976). *Icarus* **28**, 179.
Fanale, F. P. and Cannon, W. A. (1974). *J. geophys. Res.* **79**, 3397.
Huguenin, R. L. (1973a). *J. geophys. Res.* **78**, 8481.
Huguenin, R. L. (1973b). *J. geophys. Res.* **78**, 8495.
Huguenin, R. L. (1974). *J. geophys. Res.* **79**, 3895.
Huguenin, R. L. (1976). *Science* **192**, 138.
Kong, T. Y. (1976). Ph.D. Thesis in preparation, Harvard University.
Liu, S. C. and Donahue, T. M. (1976). *Icarus* **28**, 231.
McElroy, M. B. (1972). *Science* **175**, 443.
McElroy, M. B. and Donahue, T. M. (1972). *Science* **177**, 986.
McElroy, M. B. and Hunten, D. M. (1969). *J. geophys. Res.* **74**, 5807.
McElroy, M. B. and Kong, T. Y. (1976). Submitted to *Geophys. Res. Lett.*
McElroy, M. B. and McConnell, J. C. (1971). *J. atmos. Sci.* **23**, 879.
Sagan, C., Toon, O. B. and Gierasch, P. J. (1973). *Science* **181**, 1045.
Stewart, A. I. (1972). *J. geophys. Res.* **77**, 54.
Strickland. D. J., Thomas, G. E. and Sparks, P. R. (1972). *J. geophys. Res.* **77**, 4052.
Ward, W. R. (1973). *Science* **181**, 260.
Young, L. D. G. (1971). *J. Qt. Spec. Rad. Trans.* **11**, 385.

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 $\frac{^{13}C}{^{12}C}$, and $\frac{^{18}O}{^{16}O}$ 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.