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A Coupled Soil–Atmosphere Model of H_2O_2 on Mars

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The Viking Gas Chromatograph Mass Spectrometer failed to detect organic compounds on Mars, and both the Viking Labeled Release and the Viking Gas Exchange experiments indicated a reactive soil surface. These results have led to the widespread belief that there are oxidants in the martian soil. Since H_2O_2 is produced by photochemical processes in the atmosphere of Mars, and has been shown in the laboratory to reproduce closely the Viking LR results, it is a likely candidate for a martian soil oxidant. Here, we report on the results of a coupled soil/atmosphere transport model for H_2O_2 on Mars. Upon diffusing into the soil, its concentration is determined by the extent to which it is adsorbed and by the rate at which it is catalytically destroyed. An analytical model for calculating the distribution of H_2O_2 in the martian atmosphere and soil is developed. The concentration of H_2O_2 in the soil is shown to go to zero at a finite depth, a consequence of the nonlinear soil diffusion equation. The model is parameterized in terms of an unknown quantity, the lifetime of H_2O_2 against heterogeneous catalytic destruction in the soil. Calculated concentrations are compared with a H_2O_2 concentration of 30 nmoles/cm^3, inferred from the Viking Labeled Release experiment. A significant result of this model is that for a wide range of H_2O_2 lifetimes (up to 10^5 years), the extinction depth was found to be less than 3 m. The maximum possible concentration in the top 4 cm is calculated to be ~240 nmoles/cm^3, achieved with lifetimes of greater than 1000 years. Concentrations higher than 30 nmoles/cm^3 require lifetimes of greater than 4.3 terrestrial years. For a wide range of H_2O_2 lifetimes, it was found that the atmospheric concentration is only weakly coupled with soil loss processes. Losses to the soil become significant only when lifetimes are less than a few hours. If there are depths below which H_2O_2 is not transported, it is plausible that organic compounds, protected from an oxidizing environment, may still exist. They would have been deposited by meteors, or be the organic remains of past life. © 1994 Academic Press, Inc.

1. INTRODUCTION

One of the most striking results from the Viking Lander missions to Mars was the lack of organic compounds found at the surface. The Gas Chromatograph Mass Spectrometer (GCMS) showed that no organics were present in the martian soil at levels of parts per billion for complex organics, and parts per million for simple ones (Biemann *et al.* 1977, 1979). Even with the absence of life or the organic remains of life, this result is surprising. Organics should be supplied to the martian surface by meteoric infall, or could have been produced by an early reducing atmosphere and stored in subsurface reservoirs (Sagan *et al.* 1989). Recently, Flynn (1993) has estimated the flux of organic carbon on Mars to be approximately 5×10^{-18} g cm^{-2} sec^{-1}. This is based on the assumption that 10% of the interplanetary dust flux is organic carbon and that carbonaceous material not subjected to a pyrolysis temperature of 900 K (Chyba *et al.* 1990) reaches the surface intact. The absence of detected organics near the surface implies the active destruction of these molecules, either photochemically or through oxidizing agents in the soil (Klein 1979). The oxidizing nature of the martian soil has also figured prominently in discussions of future explorations of Mars. The putative oxidants may be responsible for the destruction of organic material to considerable depth, thus precluding the recovery of reducing material that may be relics of early biological forms. Additionally, there have been serious expressions of concern regarding the effect that soil oxidants may have on materials used in robotic missions and on health and safety during human missions (Coulter 1987). The concern has centered on possible irritation of the respiratory system due to dust carried into the martian habitat through air locks.

In this paper, we consider the production, transport, and destruction of an important possible martian soil oxidant, H_2O_2. A one-dimensional coupled soil–atmosphere model is developed to investigate the possible extent and concentration of H_2O_2 in the martian environment. Data from the Viking biology experiments and from laboratory

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TABLE I
A Comparison of GEx O_2 and LR ^{14}C Results (after Klein 1978)

Sample	GEx O_2 (nmol cm^{-3})	LR CO_2 (nmol cm^{-3})
Viking 1 (surface)	770	~30
Viking 2 (surface)	194	~30
Viking 2 (subrock)	70	~30

experiments that followed are used to constrain the model through appropriate boundary conditions. Our goal is to estimate the depth of the H_2O_2 oxidizing layer, as well as to point out the sensitivity of this result to the various assumptions and parameters used in the model. Furthermore, we would like to show to what degree the soil is a sink for atmospheric H_2O_2, in order to assess the significance of surface interactions to atmospheric photochemical models.

The results of the Viking biology experiments have led to the widespread belief that there are oxidants in the martian soil. The key results upon which this hypothesis is based are (see Klein 1978, Mazur *et al.* 1978, Huguenin 1982 for detailed reviews):

- The GCMS failed to detect organics in surface samples and from samples below the surface (the maximum depth sampled was about 10 cm) (Biemann *et al.* 1977, Biemann, 1979). Since there are at least two mechanisms that could produce organics on Mars, meteoritic infall and UV production (Biemann *et al.* 1977), the absence of organics suggests that a mechanism for destroying them is present.
- The soil released O_2 upon humidification in the Gas Exchange experiment (Oyama and Berdahl 1977, 1979) in amounts ranging from 70 to 770 nmoles cm^{-3} (see Table I). The O_2 was released rapidly within the first few hours after humidification; it then gradually tapered off and ceased. Heating of the sample to 145°C for 3.5 hr reduced the amount of O_2 released by about 50% but did not eliminate it, indicating that biological activity was not involved. No additional O_2 evolved when the samples were wetted with a nutrient solution but there was a slow evolution of CO_2, indicating the oxidation of organics in the medium by an oxidizing agent.
- In the labeled release experiment, $^{14}CO_2$ was rapidly released when martian surface samples were wetted with an aqueous nutrient medium containing ^{14}C-labeled organic compounds. The kinetics of the initial $^{14}CO_2$ release were similar to the initial O_2 release in the GEx humid mode tests. After the initial release tapered off (70 hr), $^{14}CO_2$ continued to evolve slowly until the experiment ended. The total abundance of CO_2 produced during the rapid response was suggestive of a nearly total reaction with only one component (formate) of the nutrient medium. A second injection of nutrient medium caused some 30% of the $^{14}CO_2$ gas to readsorb, followed again by its gradual release. The rapid $^{14}CO_2$ release was completely removed by heating at 160°C for 3 hr, partially destroyed at 40–60°C, and unaffected by storage for short periods at 18°C but lost after 2 to 4 months' storage at 18°C.

H_2O_2 is a good candidate for the thermally labile oxidant that produced the rapid evolution of CO_2 in the LR experiment. Hunten (1979, 1987) has suggested that H_2O_2 is produced in the atmosphere by photochemical reaction at a rate of about 2×10^9 molecules cm^{-2} sec^{-1} and that this could be the source of the LR oxidants. Oyama and Berdahl (1979) duplicated the response of the LR experiment by reacting formate with H_2O_2 and γFe_2O_3 mixed with a suite of possible martian surface minerals. They also duplicated the slow CO_2 production in the LR and GEx wet cycle with a mixture of γFe_2O_3 and formate. Ponnamperuma *et al.* (1977) also found that $^{14}CO_2$ was produced when the Viking LR nutrient mixture was added to γFe_2O_3 that had been irradiated with ultraviolet light under a Mars analog gas mixture. Heat pretreatment at 160°C reduced but did not eliminate the effect. They suggested that H_2O_2 may have been formed during irradiation which then reacted with formate in the medium. However, in other simulations, Levin and Straat (1981) found that H_2O_2 reacted with other compounds in the nutrient medium besides formate. Thus the H_2O_2 hypothesis does not account for the fact that only one component in the LR nutrient medium was oxidized to CO_2 in the initial fast reaction. Furthermore, Levin and Straat (1981) argue that H_2O_2 is much more thermally labile than the oxidant that produced the LR result.

In addition to photochemical formation of H_2O_2 in the atmosphere, Huguenin *et al.* (1979) and Huguenin (1982) have suggested that chemisorbed H_2O_2 is produced by frost weathering of olivine. Experiments with frost weathered olivine (Huguenin *et al.* 1979, Hugeunin 1982) reproduced the release of O_2 upon humidification (GEx result) and the oxidation of labeled formate solution to CO_2 (LR result), although the magnitude of the response was much larger than seen on Mars. Huguenin *et al.* (1979) argued that the similar kinetics of the release of CO_2 in the LR and O_2 in the GEx experiments suggests that the same active agent is responsible for both reactions and proposed that the GEx reaction was caused by the catalytic dissociation of H_2O_2 in the presence of iron catalyst and water. They further argued that the chemisorbed H_2O_2 would decay in the heat sterilization procedure to adsorbed O_2, which was desorbed upon humidification.

However, they did not demonstrate the heat sensitivity of these results experimentally.

In order to estimate the extent of the oxidized layer, and to evaluate the possible hazard that soil oxidants might pose to future missions, a standard model of martian soil oxidants is needed. Such a model should have a clear mechanism for formation on Mars and should be consistent with the Viking biology experiment results. In this vein, H_2O_2 has emerged as a "standard" martian oxidant due to its formation in the atmosphere (Hunten 1979) and in the soil (Huguenin 1982) and its ability to reproduce the LR results, including their temperature sensitivity (Klein 1978, 1979; Levin and Straat 1979). The concentration required to explain the LR results is about 1 ppm by mass. The arguments against H_2O_2 as the soil oxidant include: (1) It has a short lifetime, 10^4 sec, against UV destruction on the martian surface. (2) It alone cannot explain the thermally stable GEx results. In the next section, we further develop the standard model and propose it as a useful benchmark pending more definitive information on the true nature of the soil oxidant.

We investigate the diffusion and catalytic destruction of H_2O_2 in the martian soil to determine whether its concentration is consistent with the results of the Viking LR experiment. It is assumed that H_2O_2 is produced in the atmosphere by photochemical reactions (Hunten 1979) and diffuses into the soil. The H_2O_2 must be sufficiently mobile that it diffuses to depth before being photochemically destroyed by surface UV light. We expect that the primary sink for H_2O_2 is decomposition to water, probably catalyzed by the iron-rich soil grains. The depth of the oxidizing soil and the concentration of oxidant at the surface will depend on the degree to which H_2O_2 is adsorbed onto soil grains and on the catalytic destruction rate of the H_2O_2.

In the absence of the consideration of diffusion, adsorption, and catalytic destruction of H_2O_2 in the martian soil, atmospheric photochemical models (Hunten 1987, Kong and McElroy 1977) are only able to estimate a flux of H_2O_2 into the soil. Kong and McElroy (1977) considered several *ad hoc* assumptions regarding the effectiveness of the soil as a sink for H_2O_2 but did not attempt to quantify soil concentrations. Chyba *et al.* (1989) reported on a simple calculation of possible depths of H_2O_2 in the martian regolith, but did not consider the effect of adsorption and its feedback on deposition from the atmosphere and diffusion to depth. We concluded from these investigations that in order to treat the problem of the depth to which H_2O_2 may penetrate, a coupled soil–atmosphere transport model would be necessary.

Presented here is an analytical model that predicts atmospheric and soil concentrations of H_2O_2 based on a net flux of H_2O_2 into the soil and on adapting empirically derived adsorption isotherms for water on clean basalt under martian conditions (Fanale and Cannon 1971). The calculations are made for steady-state isothermal conditions at an average Mars surface temperature of 215 K. Concentrations in the atmosphere are determined from a simple mass balance equation and an exponential lapse rate. Concentrations in the soil are determined from a diffusion equation that incorporates catalytic destruction of adsorbed H_2O_2. Since diffusion is accomplished by the vapor phase, the adsorption isotherms are used to establish phase partitioning between the adsorbed (fixed) and vapor (mobile) phases. The soil diffusion equation is coupled to the atmoshpere equation through a flux boundary condition at the soil–atmosphere interface. The net flux of H_2O_2 into the soil is established by the atmospheric concentration at the surface as well as by soil diffusion and loss processes. Similarly, atmospheric concentrations are dependent upon both atmospheric and soil processes.

In order to uniquely determine a solution, the model requires that atmospheric production and loss rates, as well as soil loss and diffusion rates, be known. In addition, the equilibrium partitioning between H_2O_2 phases must be known. The least well determined of these is the loss rate of adsorbed H_2O_2 due to heterogenous catalysis. The lifetime of H_2O_2 adsorbed in the soil is therefore taken as a free parameter, and the general solution with respect to this parameter may be calculated.

2. THE MODEL

The model is composed of two coupled partial differential equations for the atmosphere and soil. Coupling is through a flux boundary condition at the soil–atmosphere interface, and must be consistent with atmospheric and soil concentrations. The phase partitioning between adsorbed and vapor phase H_2O_2 enters in the soil equation.

2.1. *Atmospheric Production*

Hydrogen peroxide is produced in the martian atmosphere through the combination of two hydroperoxyl radicals,

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2,$$

with a rate constant $k = 5.5 \times 10^{-12}$ cm^3 sec^{-1} (DeMore 1985). The production rate is calculated from

$$\frac{d[H_2O_2]}{dt} = [HO_2][HO_2]k.$$

Using a value of 6.5×10^7 cm^{-3} for the number density of HO_2 and a scale height, H, of 18 km (Kong and McElroy 1977), the column production rate of H_2O_2 is

$$P = H[HO_2]^2k = 4.18 \times 10^{10}\,\mathrm{cm}^{-2}\,\mathrm{sec}^{-1}.$$

2.2. *Atmospheric Loss*

The loss of H_2O_2 in the martian atmosphere is due primarily to UV radiation at wavelengths below 3750 Å, through photodissociation

$$H_2O_2 + h\nu \rightarrow 2OH,$$

with a rate coefficient (Shimazaki 1989) of

$$l = 2.5 \times 10^{-5}\,\mathrm{sec}^{-1}.$$

A simple calculation with these production and loss rates should yield an estimate of the atmospheric concentration at the surface, assuming a standard lapse rate, perfect mixing, and no losses to the soil,

$$n_a(0) = \frac{P}{lH} = 9.3 \times 10^8\,\mathrm{cm}^{-3},$$

which is in rough agreement with the number density calculated by Kong and McElroy (1977), $2 \times 10^9\,\mathrm{cm}^{-3}$, using a more sophisticated photochemical model.

2.3. *The Atmosphere Equation*

If N_a is the column density of H_2O_2 in the martian atmosphere,

$$\frac{dN_a}{dt} = P - lN_a - F_i + F_o, \tag{1}$$

where F_i and F_o are the fluxes into and out of the soil, respectively. The atmosphere is assumed to be isothermal, with an exponential lapse rate and perfect mixing

$$n_a(z) = n_a(0)e^{-z/H},$$

where $n_a(z)$ is the number density of H_2O_2 as a function of altitude and H is the density scale height. Since we are interested in the long-term equilibrium distribution of H_2O_2 Eq. (1) is solved in the steady state. The flux into the soil is assumed to be the rate at which molecules impinge upon the surface due to the thermal motion. If c is the average molecular speed, the flux into the soil is

$$F_i = \frac{1}{4}cn_a(0).$$

The flux out of the soil is similarly calculated, but is proportional to $n_v(0)$, the vapor phase concentration of H_2O_2 in the pore spaces near the surface:

$$F_o = \frac{1}{4}cn_v(0).$$

Therefore, the net flux of H_2O_2 into the soil is

$$F = F_i - F_o = \frac{1}{4}cn_a(0) - \frac{1}{4}cn_v(0).$$

The net flux is represented mathematically through a discontinuity in the number density, $n_a(0) - n_v(0)$, but it may also be related to the usual expression for diffusive transport, Fick's Law,

$$F = -D\frac{\partial n}{\partial z}.$$

The abrupt change in number density may only be "felt" by molecules within a mean free path of the surface. Therefore, as far as the net transport of molecules across the surface is concerned, the effective concentration gradient is

$$\frac{\partial n}{\partial z} \simeq \frac{n_v(0) - n_a(0)}{\lambda},$$

where λ is the H_2O_2 molecular mean free path. Fick's Law therefore becomes

$$F = \frac{D}{\lambda}[n_a(0) - n_v(0)].$$

The diffusion coefficient, from kinetic theory, is

$$D = \frac{1}{3}c\lambda,$$

so that

$$F = \frac{1}{3}c[n_a(0) - n_v(0)],$$

where the difference in the multiplying factor is due to the fact that molecules approach the surface from all angles, and the appropriate spatial integration yields 1/4 rather than 1/3. Solving for the atmospheric concentration at the surface,

$$n_a(0) = \frac{P + 1/4cn_v(0)}{lH + 1/4c} \tag{2}$$

2.4. *Soil Diffusion*

It is assumed that the atmosphere is in pressure equilibrium with gases in the interstitial spaces of the soil. Without an external concentration gradient, the thermal flux of molecules impinging upon the plane of the martian surface would be equal to the thermal flux of molecules reentering the atmosphere. A concentration gradient is set up in the soil, however, by diffusion of the vapor phase downward, by the adsorption of H_2O_2 onto grain surfaces, and by the subsequent catalytic destruction of the adsorbed phase. Diffusion of a gas through porous media may be modeled by two different mechanisms depending on whether the mean free path of the gas is greater or less than the average pore diameter. If pores are mostly larger than the mean free path, diffusion is dominated by molecular collisions. In this case, the diffusion coefficient is the gas–gas diffusion coefficient of H_2O_2 in CO_2 multiplied by a constant that depends upon the geometry of the soil. This transport mechanism is referred to as molecular diffusion. An analytical expression for the diffusion coefficient is obtained by modeling the pores in the soil as randomly twisted and distributed tubes embedded in a cross section of the soil (Ball 1981). Porosity is defined as the ratio of the pore space volume to total volume. The porosity of the martian soil is usually taken to be 0.5 (Fanale *et al.* 1986). Tortuosity is the ratio of total tube length to length projected onto a preferred axis (the direction of the flux). An average over an appropriate ensemble of tortuous tubes is used to characterize a given soil. The value used for most soils and thus for Mars is 5 (Satterfield 1970, Smoluchowski 1967). The molecular diffusion coefficient is given analytically as $D_m = (\varepsilon/\tau)D_0$ where D_0 is the gas–gas diffusion coefficient, ε is the soil porosity, and τ is the soil tortuosity (Flood 1967). The value of the molecular diffusion coefficient for H_2O_2 in CO_2 at an average surface temperature of 215 K is $D_m = 3.4$ cm^2 sec^{-1}.

If pores are mostly smaller than the mean free path, molecular collisions with the pore walls dominate the transport of H_2O_2, a process known as Knudsen diffusion. The average pore size may be very roughly taken to be about 1 μm (Fanale *et al.* 1986). The mean free path is calculated for a Mars average surface temperature of 215 K. From the kinetic theory of ideal gases, it is found to be about 27.8 μm. Therefore, Knudsen diffusion is the dominant transport mechanism for H_2O_2 through the martian soil at this temperature. The Knudsen diffusion coefficient is given analytically as $D_K = (4(\varepsilon r_0/\tau)[(2kT/\pi m)]^{1/2}$, where r_0 is the average pore radius and m is the H_2O_2 molecular mass (Clifford and Hillel 1983). The value of the Knudsen diffusion coefficient for H_2O_2 in the martian soil is calculated to be $D_K = 0.24$ cm^2 sec^{-1}. The diffusion coefficient appropriate to the conditions considered here may be derived by employing the Bosanquet approximation, where $D^{-1} = D_m^{-1} + D_K^{-1}$, and is found to be $D = 0.22$ cm^2 sec^{-1}.

2.5. *Soil Loss*

One approach to determining the chemical lifetime of the soil oxidant is based upon the observed disappearance of the active agent in the LR experiment after 82 days of storage at 18°C. Levin and Straat (1979) used the observed decline in oxidant activity to infer activation energies of about 35–43 kcal mole^{-1}. This is much larger than typical activation energies for heterogeneous catalysis but is approximately the activation energy (40–50 kcal mole^{-1}) for self-catalysis of H_2O_2 at high temperatures (over 750 K; Schumb *et al.* (1955)). Chyba *et al.* (1989) have used this activation energy to compute a chemical lifetime for H_2O_2 in the martian soil of 10^5 to 10^7 years. Laboratory work on the catalytic destruction rate of H_2O_2 in a ferrous environment, however, indicates much shorter lifetimes, on the order of minutes (Schumb *et al.* 1955). Because of the uncertainty of the actual chemistry of the martian surface, catalytic destruction rates for H_2O_2 under martian conditions are poorly constrained. The model is solved for a wide range of lifetimes in order to assess the sensitivity of soil concentrations and atmospheric losses to differences in soil H_2O_2 lifetimes.

2.6. *Phase Partitioning*

The relative concentrations of vapor to adsorbed phase H_2O_2 are calculated from an expression empirically derived by Fanale and Cannon (1971). The data was taken for the adsorption of H_2O onto clean basalt surfaces for concentrations several orders of magnitude higher than those expected for H_2O_2 adsorbed onto martian soil grains. Nevertheless, since the dipole moment and heat of fusion per gram of H_2O_2 are similar to those of H_2O (Weast 1974), we will use the Fanale and Cannon isotherms as a starting point to estimate H_2O_2 phase partitioning under martian conditions. The adsorption data is represented by an expression that gives the number of grams of H_2O_2 adsorbed per gram of soil as a function of temperature and partial pressure. The expression is

$$\rho_a = \gamma P^{B_o} e^{-\delta/T},$$

where γ, B_o, and δ are the empirically derived coefficients with values $\gamma = 6.316 \times 10^{-9}$, $B_o = 0.51$, and $\delta = 2679.8$ K. Using the ideal gas law and converting this to number densities,

$$n_c(z) = S(T) n_v^{B_o},$$

where $n_c(z)$ is the number density of the adsorbed phase,

$n_v(z)$ is the number density of the vapor phase, and $S(T)$ incorporates all the temperature dependence of the isotherm data. In adapting these isotherms, we use the mass of H_2O_2 rather than H_2O, and use a value for the exponent of 0.5, rather than the measured value of 0.51. Then the phase partitioning function is

$$n_c(z) = S(T)n_v^{1/2}, \tag{3}$$

where, using $\rho_{soil} = 1.3$ g cm^{-3} (Moore *et al.* 1977), at 215 K,

$$S(215) = 4.757 \times 10^{12} \text{ cm}^{-3/2}.$$

For a soil that is a poor atmospheric sink, the amount of adsorbed H_2O_2 may be estimated, assuming that H_2O_2 in the soil pore spaces is in equilibrium with the atmosphere ($n_v(0) \simeq n_a(0) = 9.3 \times 10^8$ cm^{-3}):

$$n_c = S(T)n_v^{1/2} = 240 \text{ nmoles cm}^{-3}.$$

This represents a maximum amount of H_2O_2 at the surface, assuming that soil losses are negligible.

For the purpose of comparing the Viking LR experiment results with the model, the surface concentration is considered to be an average over the depth to which the martian soil was sampled. This depth is taken to be 4 cm (Klein *et al.* 1976). The maximum possible concentration of H_2O_2 consistent with atmospheric–soil equilibrium was shown to be a factor of 10 higher than that measured by Viking. Therefore, soil diffusion and loss rates that do not deplete the surface by more than a factor of 10 will still be consistent with the Viking LR experiment results.

In addition to solving the model in terms of the lifetime parameter, three cases are specifically considered. The model is solved in the Density Case by constraining the average surface concentration in the top 4 cm to be 30 nmoles cm^{-3}. When the model is constrained in this way to be consistent with the Viking LR experiment results, we wish to see what lifetime is necessary to achieve such a steady-state surface concentration. We also wish to know how much of a sink the soil is for atmospheric H_2O_2 under such constraints. The model is solved in the Lifetime Case for a lifetime of 10^5 years. By considering the adsorbed H_2O_2 to be relatively stable on Mars, we would like to calculate the average surface concentration in the top 4 cm and again find to what degree the soil is a sink for H_2O_2. The third case examined is the Loss Regime Case. If H_2O_2 is unstable enough, soil diffusion, driven by a strong gradient, and soil losses, could be sufficient to make the soil a significant sink for atmospheric H_2O_2. The lifetime required for the martian soil and atmosphere to be sinks of equal magnitude is calculated.

2.7. *The Soil Diffusion Equation*

For the soil diffusion equation, catalytic destruction of adsorbed H_2O_2 is characterized by the lifetime τ. The diffusion equation is then

$$\varepsilon\frac{\partial n_v(z,t)}{\partial t} + \frac{\partial n_c(z,t)}{\partial t} = -\frac{\partial F(z,t)}{\partial z} - \frac{n_c(z,t)}{\tau}, \tag{4}$$

where ε is the porosity of the soil and F is the flux. Transport in the soil proceed by diffusion, given by Fick's Law,

$$F(z,t) = -D\frac{\partial n_v(z,t)}{\partial z},$$

where D is the diffusion coefficient. Applying this to the diffusion term, and the phase partitioning to the loss term, the steady state soil diffusion equation is

$$\frac{d^2n_v}{dz^2} = \frac{S(T)}{D\tau}n_v^{1/2}, \tag{5}$$

with boundary conditions

BC 1 $\lim_{z \text{ large}} F(z) = 0$ and $\lim_{z \text{ large}} n_v(z) = 0$

BC 2 $-D\left.\frac{dn_v}{dz}\right|_{z=0} = F_i - F_o,$

where the flux boundary condition couples to the atmosphere equation through

$$F_i - F_o = \frac{1}{4}cn_a(0) - \frac{1}{4}cn_v(0).$$

The nonlinear soil diffusion Eq. (5) may be integrated once, by multiplying by dn/dz and assuming constant temperature, to give

$$\frac{dn_v}{dz} = \pm\left[\frac{4S}{3D\tau}n_v^{3/2} + C_1\right]^{1/2}.$$

2.8. *Boundary Condition 1*

At some depth, we expect $n_v \rightarrow 0$. We also expect the gradient to go to zero. Therefore, applying the first boundary condition implies that $C_1 = 0$. Then the concentration gradient becomes

$$\frac{dn_v}{dz} = \pm \frac{2}{\sqrt{3}} \left(\frac{S}{D\tau}\right)^{1/2} n_v^{3/4}. \tag{6}$$

It is expected that the concentration will decrease with depth. Therefore the gradient is negative. We may integrate again to obtain

$$n_v(z) = \left[C_2 - \left(\frac{S}{12D\tau}\right)^{1/2} z\right]^4,$$

where C_2 may be identified as $n_v^{1/4}(0)$ and must be determined from the second boundary condition. Since we are interested in the concentration of adsorbed H_2O_2, we use the phase partitioning function, Eq. (3), to express the general solution to the soil diffusion equation in terms of the adsorbed phase concentration,

$$n_c(z) = \left[n_c^{1/2}(0) - \left(\frac{S^2}{12D\tau}\right)^{1/2} z\right]^2. \tag{7}$$

2.9. Boundary Condition 2

From Eq. (6), the net flux of H_2O_2 into the soil is, in terms of the second boundary condition,

$$-D\left.\frac{dn_v}{dz}\right|_{z=0} = \left(\frac{4S}{3D\tau}\right)^{1/2} n_v^{3/4}(0) = F_i - F_o,$$

in terms of atmospheric production and loss terms,

$$\left(\frac{4S}{3D\tau}\right)^{1/2} n_v^{3/4}(0) = P - lHn_a(0).$$

Equation (2) for $n_a(0)$, derived from the steady-state atmosphere equation is substituted into the above equation

$$\left(\frac{4S}{3D\tau}\right)^{1/2} n_v^{3/4}(0) = P - \frac{(lHP + (lH/4)cn_v(0))}{\left[lH + \frac{1}{4}c\right]}.$$

Again, since we are interested in concentration of adsorbed H_2O_2 the phase partitioning function, Eq. (3), is used to convert to a polynomial in $n_c(0)$,

$$n_c^2(0) + n_c^{3/2}(0)\left(\frac{64DS^2}{3c^2\tau}\right)^{1/2}\left[1 + \frac{c}{4lH}\right] - \frac{PS^2}{lH} = 0, \tag{8}$$

which is solved numerically.

Applying the second boundary condition has allowed us to calculate the adsorbed phase concentration for given lifetimes. The depth profile of H_2O_2 in the soil is given by the general solution, Eq. (7). Other physically significant quantities may also be calculated from $n_c(0)$. They are presented in the following sections.

2.10. Extinction Depth

The general solution to the soil diffusion Eq. (7), shows that the concentration of adsorbed H_2O_2 goes to zero at a finite depth. Due to the nonlinear phase partitioning, $n_c = S(T)n_v^{1/2}$, as the concentration of mobile H_2O_2 decreases with depth, the concentration of adsorbed H_2O_2 decreases at the square of this rate. The result is a rapid decrease in adsorbed H_2O_2 with depth. If we denote the depth at which the concentration goes to zero as z_e, the extinction depth, then for $n_c(z_e) = 0$ is given by,

$$n_c^{1/2}(0) - \left(\frac{S^2}{12D\tau}\right) z_e = 0.$$

So that the extinction depth is

$$z_e = \left(\frac{12D\tau}{S^2}\right)^{1/2} n_c^{1/2}(0). \tag{9}$$

2.11. Average Surface Concentration

The physically observable concentration of H_2O_2 in the soil at the surface is the average of $n_c(z)$ over some depth. In the Viking Biology Experiments, the sample depth was approximately 4 cm (Klein *et al.* 1976). If the depth of the layer is z_l and the average concentration in this layer is n_l, then

$$n_l = \frac{1}{z_l}\int_0^{z_l} n_c(z)dz \quad z_l \leq z_e.$$

Since the concentration of adsorbed H_2O_2 extinguishes at some depth, z_e, the limits of this integration are valid only for $z_l < z_e$. For shallow extinction depths, where $z_l \geq z_e$, the average surface concentration becomes

$$n_l = \frac{1}{z_l}\int_0^{z_e} n_c(z)dz \quad z_l \geq z_e.$$

Performing the integration, the average concentration of adsorbed H_2O_2 in the top 4 cm of soil is

$$n_l = \begin{cases} \left(\frac{4D\tau}{3S^2}\right)^{1/2} \frac{n_c^{3/2}(0)}{z_l} & z_l \geq z_e \\ \left(\frac{4D\tau}{3S^2}\right)^{1/2} \frac{n_c^{3/2}(0)}{z_l}\left[\left(\frac{z_l}{z_e} - 1\right)^3 + 1\right] & z_l < z_e. \end{cases} \tag{10}$$

2.12. *Atmospheric Number Density*

Equation (2) for the atmospheric number density at the surface may be expressed in terms of the H_2O_2 adsorbed phase concentration in the soil via the phase partitioning function, Eq. (3),

$$n_a(0) = \frac{P + \frac{1}{4}\frac{c}{S^2}n_c^2(0)}{lH + \frac{1}{4}c}. \tag{11}$$

Here, the atmospheric number density may be seen to explicitly depend upon both atmospheric and soil processes.

2.13. *Net Flux into the Soil*

The net flux into the soil is given by the second boundary condition to the soil diffusion equation,

$$F_{\text{soil}} = F_i - F_o = \left(\frac{4DS}{3\tau}\right)^{1/2} n_v^{3/4}(0).$$

Once again, this quantity may be expressed in terms of the adsorbed phase concentration of H_2O_2 through the phase partitioning function, Eq. (3),

$$F_{\text{soil}} = \left(\frac{4D}{3\tau S^2}\right)^{1/2} n_c^{3/2}(0). \tag{12}$$

This completes the general solution to the model and allows us to compute the concentration depth profile, the average concentration in the soil at the surface, the atmospheric number density at the surface, and the net flux of H_2O_2 into the soil, in terms of the soil lifetime parameter.

3. RESULTS

3.1. *Density Case*

If it is assumed that H_2O_2 was responsible for the evolution of CO_2 in the Viking Labeled Release experiment, a lower bound for the average concentration of H_2O_2 in the top 4 cm may be taken to be about 30 nmoles cm^{-3}. This concentration is achieved in the model with a H_2O_2 lifetime in the soil of

$$\tau = 1.35 \times 10^8 \text{ sec} = 4.3 \text{ terrestrial years},$$

calculated from Eq. (10). The extinction depth is calculated from Eq. (9) to be

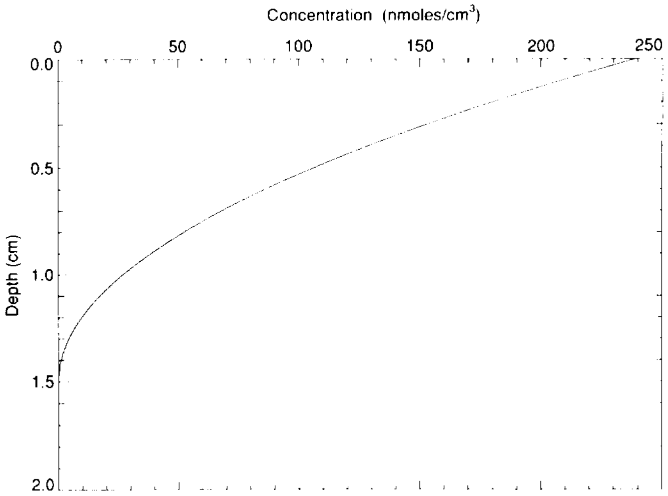

FIG. 1. The calculated depth profile of H_2O_2, with the average surface concentration in the top 4 cm constrained to be 30 nmoles/cm^3. Due to the combined effects of diffusion and catalytic destruction of adsorbed H_2O_2, the concentration is seen to go to zero at a finite depth—approximately 1.5 cm. The model predicts an average lifetime of H_2O_2 in the soil of 4.3 terrestrial years for this case.

$$z_e = 1.50 \text{ cm}.$$

Concentration as a function of depth for this case is plotted in Fig. 1. The atmospheric number density at the surface is calculated from Eq. (11) to be

$$n_a(0) = 9.170 \times 10^8 \text{ cm}^{-3}.$$

This may be compared with the number density that is obtained with the assumption that the soil is not a sink for H_2O_2,

$$n_a = 9.295 \times 10^8 \text{ cm}^{-3}.$$

It can be seen that with an average surface concentration of 30 nmoles cm^{-3}, the lifetime of 4.3 years yields a very shallow depth and a soil that is a poor sink for H_2O_2.

3.2. *Lifetime Case*

Assuming H_2O_2 to be responsible for the Viking Labeled Release experiment results, Chyba *et al.* (1989) calculated the lifetime against catalytic destruction in the soil to be about 10^5 years. Taking this as the constraint in the model, rather than average surface concentration, the same physical quantities are directly calculated. The resulting average concentration of H_2O_2 in the top 4 cm is found to be

$$n_l = 236.6 \text{ nmoles cm}^{-3}.$$

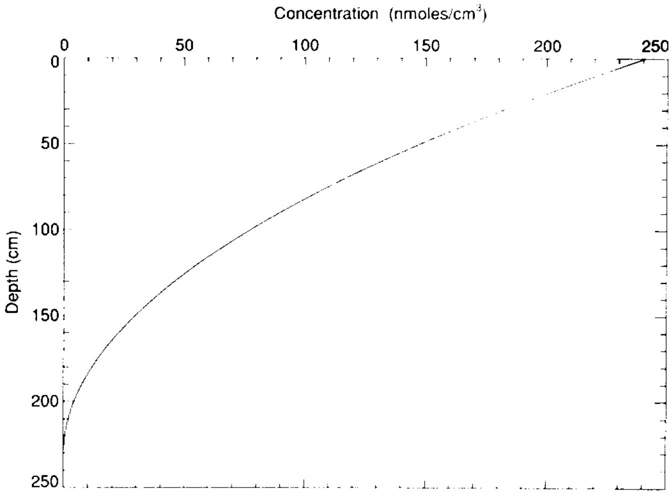

FIG. 2. The calculated depth profile of H_2O_2, with the lifetime in the soil constrained to be 10^5 years. Although H_2O_2 penetrates to greater depths than when the lifetime is 4.3 years, it can be seen that the extinction depth is still shallow—approximately 2.3 m. The average concentration of H_2O_2 in the top 4 cm is calculated in this case to be 236.6 nmoles/cm^3.

The maximum possible surface concentration was shown to be 240 nmoles cm^{-3}, so it can be seen that a lifetime of 10^5 years results in a surface concentration that is close to the asymptotic limit. The extinction depth is found to be somewhat deeper than for the Density Case,

$$z_e = 231.0 \text{ cm}.$$

H_2O_2 concentration as a function of depth for the Lifetime Case is plotted in Fig. 2. The atmospheric number density reflects the fact that the soil is an even weaker sink for H_2O_2,

$$n_a(0) = 9.29 \times 10^8 \text{ nmoles cm}^{-3},$$

which is within 0.1% of that obtained for a completely passive surface.

3.3. Loss Regime Case

The model results for the Density and Lifetime Cases show that for a wide range of lifetimes of H_2O_2 in the soil, the atmospheric number density is affected only slightly. However, it is interesting to explore the behavior of the model for regimes where the soil may play a more active role in the destruction of H_2O_2. By identifying these regimes, it is possible to assess the effect of assumptions about the lower boundary condition used in more complex atmospheric models. In the loss regime case, the physical quantities are calculated for the condition that the soil and atmosphere are H_2O_2 sinks of equal magnitude. This condition is met when the lifetime of H_2O_2 in the soil is

$$\tau = 8.8 \text{ hr}.$$

The resulting average surface concentration is very small,

$$n_l = 0.275 \text{ nmoles cm}^{-3}$$

and the extinction depth is very shallow

$$z_e = 3.5 \times 10^{-3} \text{ cm}.$$

Thus we see that for the soil to represent a sink for H_2O_2 that is comparable with the atmosphere, surface concentrations will be extremely small, with all the H_2O_2 residing very close to the surface in a soil that efficiently catalyses its decomposition.

4. DISCUSSION

The nonlinear relationship between adsorbed and vapor phase H_2O_2 results in a parabolic depth profile for the solution to the soil diffusion equation. This curious result implies that H_2O_2 is actually extinguished at a finite depth, rather than asymptotically approaching zero, as for a linear diffusion equation. Depth profiles for the Density and Lifetimes Cases are shown in Figs. 1 and 2, respectively. Figure 1 shows that when the model is constrained by an average surface concentration of 30 nmoles cm^{-3}, the H_2O_2 is contained in a very shallow layer near the surface, and no H_2O_2 can penetrate below 1.5 cm. The lifetime of H_2O_2 in the soil is 4.3 terrestrial years, and the soil represents only about 1% of the total sink for H_2O_2. Very shallow extinction depths are, however, argued against by the discovery of reactive soils under rocks (see Table I). It is likely, therefore, that the average surface concentration of H_2O_2 is somewhat greater than the lower bound inferred from the Viking results. Figure 2 shows that when the lifetime of H_2O_2 in the soil is constrained to be 10^5 years, the average concentration of H_2O_2 in the top 4 cm of soil is about eight times higher, at 237 nmoles cm^{-3}. Again, the H_2O_2 is confined to a shallow layer of 2.3 m near the surface. With this long a lifetime for H_2O_2 in the soil, the soil becomes a negligible sink for H_2O_2.

The soil diffusion equation is solved with a flux boundary condition at the soil–atmosphere interface, coupling it with the atmosphere mass-balance equation. In this way, given atmospheric production and loss rates, and soil loss and diffusion rates, concentrations may be predicted throughout the coupled soil–atmosphere system. Since the lifetime of H_2O_2 against heterogenous catalytic destruction under martian conditions is not well constrained, the model is characterized in terms of this parameter.

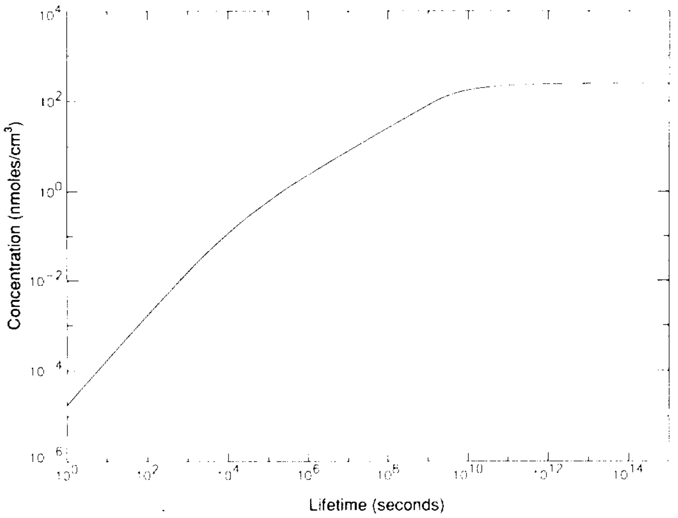

FIG. 3. The average concentration of H_2O_2 in the top 4 cm of soil, plotted against the lifetime of H_2O_2. It can be seen that for lifetimes greater than 4.3 terrestrial years, the average concentration exceeds 30 nmoles/cm^3.

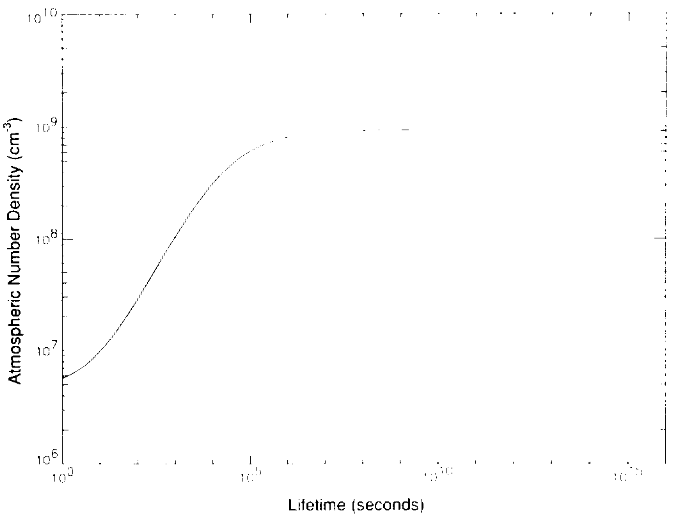

FIG. 5. Atmospheric concentration of H_2O_2 plotted as function of the lifetime of H_2O_2 in the soil. For lifetimes greater than 1 terrestrial day, soil losses do not substantially affect the concentration of atmospheric H_2O_2. As lifetimes in the soil become shorter, soil losses dominate the destruction of H_2O_2, and the overall atmospheric concentration is reduced.

Quantities of physical interest are the average concentration of H_2O_2 in the top 4 cm of soil, the extinction depth, and the atmospheric number density at the surface. These quantities are plotted as a function of the lifetime parameter in Figs. 3, 4, and 5. Figure 3 plots the average concentration of H_2O_2 calculated to be in the top 4 cm as a function of the free parameter, the lifetime of H_2O_2 in the soil. Concentrations of 30 nmoles cm^{-3}, consistent with our interpretation of the Viking LR results, are achieved with lifetimes of 4.3 terrestrial years or more. The extinction depth of H_2O_2 as a function of the lifetime parameter is plotted in Fig. 4 . The relationship is nearly linear on a log–log plot, with depths to the unoxidized layer being less than 3 m for any lifetime less than about 10^5 years. In order to demonstrate the relative strengths of the atmosphere and soil as sinks for H_2O_2, the atmospheric number density is plotted as a function of the lifetime parameter in Fig. 5. The soil becomes a significant sink with respect to the atmosphere only if lifetimes are on the order of several hours or less.

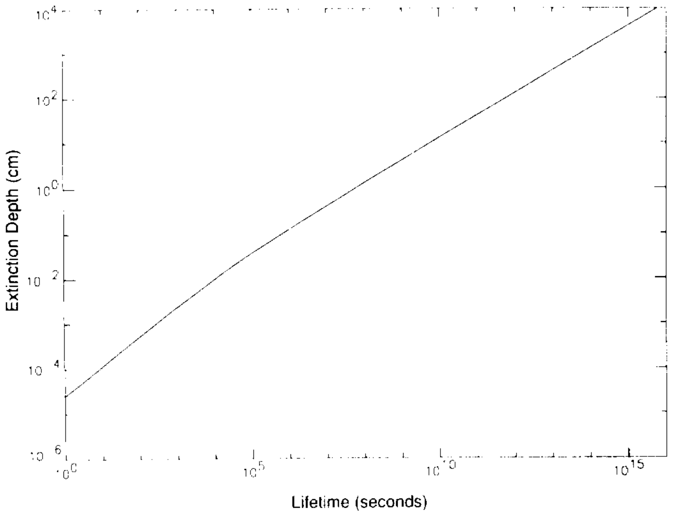

FIG. 4. The H_2O_2 extinction depth plotted as a function of the lifetime of H_2O_2 in the soil. The extinction of H_2O_2 occurs at a finite depth due to the combined effects of adsorption and catalytic destruction retarding diffusion. For all but extremely long lifetimes (greater than 10^5 years), H_2O_2 is unable to penetrate below 3 m.

A significant result of the H_2O_2 diffusion model presented here is that for a very wide range of H_2O_2 lifetimes in the soil, the oxidizing layer is confined to the top 3 m. This is due to the fact that as the partial pressure of H_2O_2 is reduced, the ratio of gas to adsorbate is also reduced. Therefore, as the mass flux drops, the role of adsorption in retarding diffusion becomes more significant. This result is dependent upon the exact form of the adsorption isotherms that are incorporated into the model. Since laboratory data on the adsorption of H_2O_2 under martian conditions is unavailable, the adaptation of laboratory-derived isotherms for water is clearly a weakness of the present model. However, simplified theoretical schemes of physical adsorption, namely Langmuir and BET isotherms, roughly exhibit the same behavior—if vapor diffusivity falls off faster than partial pressure, the resulting negative feedback will always limit H_2O_2 diffusion to a fairly shallow depth.

In calculating the results from the H_2O_2 diffusion model, we have made several assumptions with regard to the behavior of H_2O_2 in the martian soil. For the present analysis, the similarity in the dipole moments (12% difference) and heats of fusion per gram (50% difference), for H_2O and H_2O_2 serve to justify the adaptation of the laboratory-derived isotherms. Although we believe that the exact nature of H_2O_2 adsorption onto martian soil grains will not affect the basic results, a significantly better understanding of the role that H_2O_2 plays in the martian soil could be achieved through laboratory determinations of the appropriate adsorption isotherms. Similarly, laboratory measurements of the stability of H_2O_2 in Mars-like environments would be of great help in scaling the model to real Mars-like conditions.

One possible explanation for the surprising stability of H_2O_2 in the martian soil could be the observations that catalytic decomposition of peroxide is retarded at low temperatures. Solid H_2O_2 is surprisingly inert. For example (Schumb *et al.* 1955), if added carefully so as not to allow thawing, chilled 0.5 *N* permanganate solution, particles of rust, and other catalysts were found to cause no decomposition of 90 wt% H_2O_2 at $-55°C$. Decomposition began only after melting started. The applicability of these results to adsorbed layers of H_2O_2 is not clear but does suggest a possible reason for the low reaction rates.

With a model of H_2O_2 distribution in the martian soil and atmoshpere we may hope to address the following three questions:

1. Is a theoretical model of H_2O_2 transport in the martian environment consistent with the Viking Biology experiment results?
2. To what degree is the soil a sink for atmospheric H_2O_2?
3. At what depth may we expect to find an unoxidized layer, possibly containing organic compounds?

In order for the model to be consistent with some interpretation of the Viking Labeled Release experiment, we may constrain the average concentration of H_2O_2 in the top 4 cm of the soil to be at least 30 nmoles cm^{-3}. This may be achieved in the model if the lifetime of H_2O_2 in the soil is at least 4.3 terrestrial years. In this sense, the model is not inconsistent with the additional inference of a H_2O_2 lifetime of 10^5 years. Additionally, at these soil concentrations and lifetimes, we see that the soil is a poor sink for H_2O_2. Therefore, atmospheric concentrations of H_2O_2 predicted by this model are consistent with more complex atmospheric models that assume a passive surface. We may conclude that as long as the lifetime of H_2O_2 in the soil is greater than 4.3 terrestrial years, the model is consistent with Viking Biology experiment results. For any value of lifetime of H_2O_2 in the soil that is consistent with the Viking Biology experiment results, the soil is a poor sink for H_2O_2 compared with the atmosphere. Unless the lifetime is on the order of several hours or less, the atmosphere may be considered the primary sink for H_2O_2. Given this condition, more complex models of H_2O_2 production and loss in the martian atmosphere that neglect losses to the soil do so without loss of accuracy. For all lifetimes shorter than 10^5 years, the depth to complete extinction of H_2O_2 was less than 2.3 m. Although it might be expected that higher diffusion depths can be achieved by a gas, adsorption and subsequent catalytic destruction severely limit the depth to which H_2O_2 may penetrate. As Chyba *et al.* (1989) have pointed out, small-scale cratering has probably impact gardened the regolith to a depth of 5 m or more. Therefore, if H_2O_2 is the primary agent responsible for the oxidation of organics in the martian regolith, it may be inferred that the depth at which organics may still exist is not limited by the existence of H_2O_2. It is possible that organic material may remain intact beneath a shallow impact-gardened layer.

Recently, Wright *et al.* (1989) have analyzed the meteorite EETA 79001, one of the SNC meteorites believed to have originated on Mars (Becker and Pepin 1984, Bogard *et al.* 1984), and found evidence that it contains more than 400 ppm degradable organic material. The isotopic ratio of carbon in the organic material is suggestive of a biological origin, although terrestrial contamination in these measurements cannot be ruled out (Jakosky 1991). The organic material may be derived from organic bearing sediments that were laid down during an earlier, more clement period when life was widespread on the martian surface (McKay and Stoker 1989). Since SNC meteorites are thought to have resided on Mars up to 180 million years ago, and conditions on Mars that were conducive to life had disappeared by 2 billion years ago (Pollack *et al.* 1987, McKay and Stoker 1989), it is possible that the organic material seen in the meteorite was formed during an earlier epoch. Using the proposed mechanism (Melosh 1985) to explain how the SNC parent body was ejected from Mars, one can estimate the approximate depth beneath the martian surface from which the meteorite ETA 79001 originated. Because the meteorite contains organics, it presumably originated from below the oxidizing soil layer. The original depth of the material is estimated from the fact that the meteorite was not exposed to cosmic rays in space and therefore must have been shielded by a minimum of 3 m of material (Bogard *et al.* 1984). Because the meteorite material is only weakly shocked, it must have come from near the martian surface. The maximum depth of material ejected from Mars depends on the size of the impacting object that ejected it (Melosh 1985). For an impactor of 10 km, the maximum depth of the material ejected is approximately 40 m (Melosh 1985). Thus presuming that the SNC meteorites are from Mars, unoxidized organic carbon should be found at reasonably shallow depths, a few tens of meters at most. This is in agreement with the results calculated from our soil diffusion model.

For the purpose of discussing the oxidizing soil on Mars, we have adopted a "standard" model of martian soil oxidants. The results of the Viking biology experiments are assumed to be explained by the existence of three oxidants—a strong, thermally stable oxidant or adsorbed O_2 is invoked to explain the GEx results, H_2O_2 is assumed to be responsible for the rapid decomposition of organics in the LR experiment, and an additional weak oxidant is required to explain the slow continued release of CO_2 in the GEx and LR experiments (Klein 1978, 1979). The purpose of the diffusion model presented here is to explore the transport of one of these oxidants, H_2O_2 and to see to what extent it may affect the depth to an unoxidized layer. Given the assumptions of the model and the rough extrapolations from laboratory data, we find that for H_2O_2 lifetimes of less than 10^5 years, the depth to the unoxidized layer is 3 m or less.

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