THE DESTRUCTION OF ORGANIC COMPOUNDS ON MARS

A Thesis Presented To
The Faculty of the Department of Physics
San Jose State University

In Partial Fulfillment of the
Requirements for the Degree of
Master of Science

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August 1991
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Abstract

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In their search for life on the planet Mars, the Viking Landers obtained evidence of a highly oxidizing soil, and a lack of organic compounds. If life at one time existed on Mars, its organic remains may have perished due to oxidants in the soil or solar ultraviolet radiation. This thesis reports on the results of two investigations of organic destruction at the surface of Mars. In one, simulations of the martian environment were created in the laboratory for the purpose of measuring the photodegradation of amino acid. In the second a theoretical model of the distribution of H₂O₂, a potential soil oxidant, is developed for the martian environment. The laboratory investigations suggest that solar UV radiation is sufficient to destroy all organic material that may reach the martian surface through meteorites. The model of H₂O₂ distribution predicts that H₂O₂ cannot exist below depths of a meter. If H₂O₂ is the primary oxidant in the martian soil, carbon such as in meteoritic organics or the past remains of life may still exist beneath the surface.
Acknowledgements

I wish to thank Dr. Carol Stoker for her support, patience and creative suggestions during the two and one half years these projects took place. Her commitment to laboratory research in the planetary sciences, and to her students, created a truly ideal atmosphere for learning and research. I would also like to thank Dr. Christopher McKay for introducing the soil diffusion problem to me, for his guidance on physical insight, and for his encouragement. Dr. Aaron Zent contributed greatly to my understanding of the physics of soil and diffusion processes. Likewise, Dr. Tom Scattergood contributed his energies to teaching me some analytical chemistry, and enthusiastically contributed his Gas Chromatograph along with a great deal of help. My thanks go to Dr. Joseph Becker, who tirelessly steered me through the thesis process, offering suggestions, guidance, and a powerful administrative insight. Dr. Patrick Hamill also was continually supportive and helpful. The planetary science laboratory at NASA Ames Research Center is shared with Dr. David Blake and Kathy Kato, staffing the Electron Microscopy Lab. Dr. Blake never failed to offer his time, equipment and insightful advice whenever it was needed, which was frequently. Indeed, both he and Mrs. Kato created an atmosphere in the lab of communication, support and sharing. I have learned that these are elements that are required for effective laboratory research, and for making the laboratory a safe and enjoyable place to be.
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Chapter 1

Introduction

Unique among all scientific experiments were those carried out by the Viking Landers on the surface of Mars. For the first time, in situ analyses of the surface of another planetary body were made. The Viking biology experiments, in particular, analyzed the surface material of Mars for evidence of microbial life. It is widely held (Klein 1978, 1979; Oyama et al. 1977, 1978, 1979) that the results of these experiments indicate a lack of life at the surface of Mars. However, they do indicate a highly reactive surface chemistry (Klein 1978; Oyama et al. 1978). Some of the most striking results of the Viking Lander experiments were those from the Gas Chromatograph Mass Spectrometer (GCMS). The instrument was unable to detect compounds at levels of parts per billion for organics with three or more carbons, or at levels of parts per million with one or two carbon atoms (Biemann 1977, 1979). Meteoritic material is estimated to reach the martian surface at rates of between 2,700 and 202,200 metric tons per year (Flynn and McKay 1989), resulting in martian soil that is as much as 58% meteoritic debris.
Furthermore, because of Mars’ low gravity and atmospheric pressure, much of the meteoritic material may arrive unmelted. If it is assumed that organic carbon makes up 1% of large unmelted particles and 10% of small particles, the total flux of organic carbon would be in the range of $5.2 \times 10^{-5}$ and $6.9 \times 10^{-7}$ g m$^{-2}$ yr$^{-1}$. Since this source of organic carbon remained undetected, it must be concluded that it is being destroyed at rates greater than its influx. Organic compounds due to life or the past remains of life may be meeting a similar fate. The evolution of CO$_2$ from the Viking Lander Labeled Release experiment (LR) is consistent with the presence of a thermally labile oxidant such as H$_2$O$_2$ (Klein 1979), which can act to destroy organics. H$_2$O$_2$ is produced in the atmosphere (Kong and McElroy 1977; Hunten 1979), and may possibly be produced by weathering processes in the presence of iron in the soil (Huguenin 1979). The existence of alkali and alkaline earth superoxides (Oyama et al. 1976; Oyama and Berdhal 1977; Ballou et al. 1978) have been proposed to explain the evolution of O$_2$ in the Gas Exchange experiment (GEX), as well as to provide a destruction mechanism for organics. Photochemical processes have been used to suggest an explanation for the creation of oxides in the martian soil (Chun et al. 1978; Oro and Holzer 1979). In addition, there are explanations for the negative response of the GCMS that do not posit the existence of oxidants in the soil. For example, Banin and Rishpon (1979) and Banin and Margulis (1983) suggest that intrinsically reactive clays may explain the results of both the LR and GEX. Fanale et al. (1982) proposed that O$_2$ released in the GEX was desorbed from the soil. It is also possible that photochemical processes alone are responsible for the dearth of organics at the surface. Ultraviolet radiation at wavelengths as short as 2000 Å reaches the surface of Mars, producing an environment that
is probably quite hostile to organic compounds.

The question of the martian surface chemistry is unresolved, but important bounds may be placed on the rates of physical and photochemical processes involved in the destruction of organics. This thesis reports on two projects that investigate the rate of photochemical degradation of organics on Mars and the distribution of a likely candidate for an oxidant, H₂O₂. The first project is a laboratory experiment in which the soil, atmosphere and solar radiation of Mars are simulated inside glass chambers. Small quantities of amino acids are introduced into the Mars-like environment, and the degradation products and rates are determined via Gas Chromatographic analysis of the headspace gases. By scaling the UV flux to that at the martian surface, a determination of the photodegradation rate of organic compounds may be made. Considering that surface winds can expose the loose top layers of soil to solar UV radiation, it may be expected that any organics present on Mars will undergo destruction. Ultimately, the goal is to determine if photodegradation alone can explain the lack of organics found at the martian surface. The second project is the development of a model of H₂O₂ production, transport and loss through the martian environment. If H₂O₂ is the oxidant responsible for the evolution of CO₂ in the LR experiment, we would like to predict to what depths it may exist. If there are depths below which H₂O₂ cannot penetrate, there may be reason to believe that organic compounds can exist there. These organics would be from meteoritic influx, or perhaps even from the remains of past life.
Chapter 2

The Degradation of Organic Compounds Under Simulated Martian Conditions

2.1 Experimental Apparatus

Simulations of the martian environment took place in specially designed glass vessels, known as Mars Jars, shown in Figure 2.1. Each of these 350 ml containers are fitted with a greaseless stopcock to allow for the introduction and extraction of headspace gases, and a vacuum tight quartz lid. The quartz lids allow the transmission of UV radiation down to 2200 Å. Clamps and O-ring seals ensure that the vessels remain vacuum tight over the 5 week duration of the experiments, yet allow for cleaning and sterilization prior to the introduction of the Mars analog soil. Once the soil and/or amino acid has been placed
into the jars, and the jars are assembled, gas filling and flushing is accomplished with the use of a gas manifold built for this purpose. The Mars atmosphere analog was made by Scott Specialty Gases, and consists of 95.59% CO₂, 4.21% Ar, 0.11% O₂, and 0.09% CO. The Mars Jars manifold is shown in Figure 2.2.

The experiments are begun by placing the filled Mars Jars under the illumination of a 1000 Watt Conrad-Hanovia Xe short arc lamp, enclosed in a Schoeffel LH 152N lamp housing. Four Mars Jars at a time may be accommodated, providing varying levels of flux to each jar. The Xe lamp is powered by a 50 Amp Schoeffel LPS 255HR Short Arc Power Supply and ignitor. Since the Xe lamp produces an excess of infrared radiation, a specially designed IR filter, consisting of a 10 cm column of distilled water and a cooling jacket is attached to the lamp housing. A two gallon reservoir, cooled by a fan, and an aquarium pump are used to cool and circulate the water in the IR filter jacket. Due to the copious amounts of UV radiation produced by the lamp, ozone is produced along the optical path of the beam. Therefore, the entire arrangement of lamp, IR filter and Mars Jars must be operated within a fume hood. In order to operate the lamp in a vertical position, and to ensure an adequate path length for the divergence of the beam to illuminate the Mars Jars, a 6 inch first surface mirror is employed to direct the beam at a 45° angle. This arrangement is shown in Figure 2.3, which shows the equipment contained under the fume hood.

At periodic intervals the Mars Jars are removed from the beam and connected to the manifold for the extraction of headspace gases. The gases are allowed to expand into the sample bulbs, shown in Figure 2.4. These bulbs are then used for injection of the sample gases into a Perkin Elmer 900 Gas Chromatograph. The
GC is equipped with a 5 meter column, packed with Porasil C (phenylisocyanate coated glass beads) and Flame Ionization Detector (FID). The GC is shown in Figure 2.5. Hydrocarbon gas standards, supplied by Scott Specialty Gases, were used to calibrate the GC each time samples were analyzed. The output from the GC was used to drive an HP 3394A integrator for quantifying the sample gases.

2.2 Calibrations

2.2.1 Light Flux Calibration

In order to calculate the quantum efficiency of the organic degradation in the Mars simulations, an accurate calibration over the spectrum of the Xe lamp was required. To this end, 2 optical detectors were designed and built, using EG&G HUV-1100BQ photodiodes with integral operational amplifiers. One detector was designed for use with a set of Andover UV bandpass filters, in the range of 2500 to 3500 Å. The other detector was designed for the visible range, 4000 to 7000 Å, and mated with a set of Optics Technology visible bandpass filters (Set No. 3364).

The UV detector was calibrated using an Optronic Laboratories D₂ Ultraviolet Irradiance Standard, Serial No. UV-206, powered by a Hamamatsu HTV-C704 Deuterium Lamp Power Supply. The calibration was done with 2500 Å, 3000 Å, and 3500 Å UV bandpass filters for which transmission curves were supplied. The typical width at half-maximum for these filters was about 100 Å. The
published output of the D$_2$ standard lamp was integrated over the response of the UV filters in order to calculate the fluxes into the UV detector. The detector's output was measured with a Fluke 8024B digital voltmeter, and the responsivity expressed in terms of volts/µwatts for radiation at each wavelength. A similar procedure was developed for calibrating the visible detector. Typical width at half-maximum for the visible filters was 200 Å. In this case, a 1000 Watt NBS traceable tungsten filament lamp, EPI-1072, operated at 8.3 Amperes was used as the standard. Calibration curves for the two detectors are shown in Figures 2.6 and 2.7.

Once the detectors were calibrated, many measurements were made to determine the spectrum and spatial distribution of the flux at the location of the Mars Jars. The measured spectrum is shown in Figure 2.8, and measurements of the flux at various positions in the beam are shown in Figure 2.9.

2.2.2 Gas Chromatograph Calibration

The products sought in the photochemical breakdown of glycine were simple hydrocarbon gases, such as methane, ethane, ethylene and propane. For this reason, the phenylisocyante packed column and FID detector were used. The GC/Integrator combination was capable of detecting quantities of hydrocarbon gas down to concentrations of picomoles cm$^{-3}$. The volumes of the Mars Jars, sample bulbs and GC injector were accurately determined in order to perform the calculations for total amount of each hydrocarbon species produced. In addition, it was necessary to inject 2 sets of standards before and after each sample
run. A typical run involved running sets of hydrocarbon gas standards, two injections from each sample bulb, one blank injection for background subtraction, and finally two sets of standards again. By bracketing the analysis with standards and by running background blanks, the statistics for measuring the extremely small amounts of hydrocarbon gas injected were improved. Calibration of the GC involves the injection of known quantities of a known mixture of hydrocarbon gases. The integrated standard peaks produced by the integrator are shown in Figure 2.10. Using the peak areas, the sensitivity of the detector is calculated for each species. The sensitivity of the GC for each species is known as the molar response (MR), and is expressed in counts/nanomole. An example of the results of the standards calculations is shown in Table 2.3.

### 2.3 Experimental Procedures

The first steps in beginning the Mars Jars experiments involved making sure that everything in the simulation environment was chemically cleaned, sterilized, and kept contaminant free. All glassware, including the Mars Jars and sample bulbs, were rinsed with doubly distilled water, 0.1 M HCl, and then with doubly distilled water again. The vessels were completely wrapped in Al foil, and baked for 14 hours in an oven kept at 485°C. The glassware was only unwrapped immediately prior to the introduction of soil and gas. All non-glass items, such as stopcocks and O-rings were also rinsed with doubly distilled water, 0.1 M HCl, and doubly distilled water again. They were then sterilized in an autoclave prior to assembly.
The Mars analog soil, palagonite, was placed in a cleaned and sterilized container and allowed to dry under a He stream for 14 hours at 105°C. For the experiment, 2 mg of the amino acid glycine were mixed with 200 mg of the dried palagonite. The mixture was introduced into the Mars Jars, and the jars assembled and evacuated. In order to remove adsorbed gases, the jars were flushed 3 times with high purity He, to 100 mbars, and then 5 times with the Mars gas. Each time, the jars were reevacuated to 0.05 torr. Finally, the jars were filled to 100 mbar with Mars gas and placed under the calibrated Xe lamp. They were irradiated at various flux levels for periods of up to 5 weeks. Every 3 or 4 days, 5 ml amounts of headspace gas were removed for GC analysis. Each time an extraction was made, so was a flux measurement under the lamp. Also, the soil/glycine mixtures were agitated at the same intervals. After 7 to 10 such extractions, the pressure of the headspace had diminished to below 50 mbars, and the experiment was terminated.

Numerous controls were also assembled and irradiated during the course of the experiment. These were designed to provide checks on contamination and to attempt to elucidate the nature of the photodegradation process. Table 2.1 lists the Mars simulations and controls that were run over the course of the experiments.

2.4 Data Analysis

The goal of the analysis for this experiment was to convert the raw data from the GC into absolute quantities of product gases in the Mars Jars headspace.
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Mars Jar</th>
<th>Designation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1</td>
<td>High Flux</td>
<td>soil + glycine + Mars gas</td>
</tr>
<tr>
<td>I</td>
<td>2</td>
<td>Low Flux</td>
<td>soil + glycine + Mars gas</td>
</tr>
<tr>
<td>I</td>
<td>3</td>
<td>He Atmosphere</td>
<td>soil + glycine + He</td>
</tr>
<tr>
<td>II</td>
<td>4</td>
<td>High Flux</td>
<td>soil + glycine + Mars gas</td>
</tr>
<tr>
<td>II</td>
<td>5</td>
<td>He Atmosphere</td>
<td>soil + glycine + He</td>
</tr>
<tr>
<td>II</td>
<td>6</td>
<td>Soil Only</td>
<td>soil + Mars gas</td>
</tr>
<tr>
<td>III</td>
<td>7</td>
<td>High Flux</td>
<td>soil + glycine + Mars gas</td>
</tr>
<tr>
<td>III</td>
<td>8</td>
<td>Low Flux</td>
<td>soil + glycine + Mars gas</td>
</tr>
<tr>
<td>III</td>
<td>9</td>
<td>Glycine Only</td>
<td>glycine + Mars gas</td>
</tr>
<tr>
<td>III</td>
<td>10</td>
<td>Darkness</td>
<td>soil + glycine + Mars gas</td>
</tr>
</tbody>
</table>

Table 2.1: Mars Jars and Controls

The measured light fluxes into the Mars Jars are used to calculate the quantum efficiency of the glycine photodegradation. The analyses consisted of the following steps:

1. Corrections for the expansion of the sample bulb into the GC injection manifold.

2. Subtraction of the background peaks.

3. Corrections for the expansion of the Mars Jars headspace gases into the sample bulb.

4. Corrections for the repeated withdrawal of sample gases from the Mars Jars.

5. Calculations of the net amount of each product species generated, as a function of time

A chromatogram from one of the sample injections is shown in Figure 2.11.

The quantity of a gas injected into the GC column is proportional to the integrated area of the output peak. If $A$ is the area of the peak, MR is the instrument’s molar response for the gas, and $V_i$ is the injection volume, then the concentration in the injection volume is

$$n = \frac{A}{(MR)V_i}$$

In order to determine the actual quantity of a gas species in the sample bulb, a correction must be applied to account for the dilution of the sample gas when it is expanded into the GC manifold. If $V_s$ and $P_s$ are the sample bulb volume and starting pressure, $V_{gc}$ is the volume of the GC manifold, and $V_i$ is the volume injected into the column, then the resulting pressure, $P$ when the gas in the sample bulb is expanded into the manifold is:

$$P = \frac{P_s V_s}{(V_s + V_i + V_{gc})}$$

for an isothermal expansion. The concentration in the sample bulb before the expansion was

$$n_s = \frac{A}{(MR)V_i} \left(\frac{V_s + V_i + V_{gc}}{V_s}\right)$$  \hspace{1cm} (2.1)$$

For the second expansion of the sample bulb, this correction must be applied again, so that the concentration of gas before expansion (2) is

$$n_s^{(2)} = \frac{A}{(MR)V_i} \left(\frac{V_s + V_i + V_{gc}}{V_s}\right)^2$$  \hspace{1cm} (2.2)$$

The GC consistently exhibited background peaks—that is, small hydrocarbon peaks that were quantified even in the absence of sample gases. The backgrounds were directly subtracted from the integrated peak areas. Corrections
for expansion were applied after the background subtraction, to obtain corrected peak areas, $A_{corr}$, given by

$$A_{corr} = \frac{A^{(1)}}{2(MR)V_i} \left( \frac{V_s + V_i + V_{gc}}{V_s} \right) + \frac{A^{(2)}}{2(MR)V_i} \left( \frac{V_s + V_i + V_{gc}}{V_s} \right)^2 \quad (2.3)$$

where $A^{(1)}$ is the area of the peak produced by the first injection, and $A^{(2)}$ is the area of the peak produced by the second injection. All the calculations were implemented on a set of linked Microsoft Excel spreadsheets, developed for this purpose. Part of one of the spreadsheets is reproduced in Table 2.4. The corrections for background peaks and sample bulb volume expansion are applied in columns 3 and 4.

When headspace gases are transferred from the Mars Jars to the sample bulbs, a similar dilution occurs. This may be corrected for by knowing the volumes of the Mars Jars, $V_{MJ}$, the Mars Jars manifold, $V_m$, and the starting pressure in the Mars Jars, $P_{MJ}$. In terms of the concentration in the sample bulb after one extraction, the concentration of gas that had been in the Mars Jar before that extraction is

$$n_{MJ} = n_s \left( \frac{V_m + V_s + V_{MJ}}{V_{MJ}} \right) \quad (2.4)$$

For the $m^{th}$ extraction from the Mars Jar, the concentration of gas that had been in the Mars Jar before the expansion is:

$$n_{MJ}^{(m)} = n_s \left( \frac{V_m + V_s + V_{MJ}}{V_{MJ}} \right)^m \quad (2.5)$$

In order to calculate the total production of a gas species, the amount removed from the Mars Jar at each extraction must also be accounted for. These corrections are applied in the top columns 5-8 and bottom columns 3-5 of Table 2.4.
For the glycine molecule, shown in Figure 2.22, both the amino group and the carboxylic acid groups are responsible for UV absorption. Photons in the range of 2500 Å - 2100 Å are absorbed by aliphatic amines, and in the range of 2400 Å - 2300 Å by carboxylic acids (McLaren and Shugar 1964). For calculating the quantum efficiency of the photodegradation, the flux below 2500 Å is considered responsible for the destruction of glycine. Although the exact nature of the mechanism is unknown, it is assumed that the detection of one CH₄ molecule is indicative of the destruction of one glycine molecule. Knowing the area of the soil that is irradiated, $A_M$, and the measured UV flux at the position of the Mars Jar, the total flux in the range of 2000 Å to 2500 Å is calculated. The quantum efficiency of the production of a gas species is then calculated by dividing the production rate by the number of photons striking the soil per second. Examples of the results of these calculations are found in the bottom columns 6-8 of Table 2.4.

2.5 Results

Approximately 7 extractions were performed on each of the 10 Mars Jars and controls that were run. At the time of each extraction, flux measurements were also made. Plots of the total hydrocarbon production as a function of time for each of the Mars simulations and controls are shown in Figures 2.12 to 2.21. Since CH₄ was by far the most commonly observed degradation product, only results for the quantum efficiency of CH₄ are shown here. The average production rates of CH₄, UV light flux, and quantum efficiency of CH₄ production are
shown for each Mars Jar in Table 2.2. Production rate versus flux is plotted in Figure 2.23. The average quantum efficiency for the total of 42 extractions is given by the slope of plotted line. It is $1.73 \times 10^{-6}$ CH$_4$/photon.

Experimentally, a wide spread in quantum efficiencies is observed. A primary source of random experimental error is due to the precision of the GC analysis. For the extractions that were made after only a short period of irradiation, hydrocarbon concentrations in the sample bulbs were close to GC background values. For later extractions, systematic errors in the volume determinations of the manifold, Mars Jars, sample bulbs and GC injection system were compounded. These random and systematic errors conspired to produce a standard deviation of the data of 48%. A more accurate determination of the quantum efficiency of the photodegradation of glycine would require more sensitive hydrocarbon detection in the GC analysis, or substantially higher irradiation fluxes. A histogram of the quantum efficiencies for all the Mars Jars extractions is shown in Figure 2.24.

2.6 Discussion

The experimental range for the quantum efficiencies of CH$_4$ production in the Mars simulations was $0.90 \times 10^{-6}$ to $2.56 \times 10^{-6}$ molecules/photon, based on the $2\sigma$ width of Figure 2.24. Higher order hydrocarbons, such as C$_2$H$_6$, C$_2$H$_4$, and C$_3$H$_8$ were also produced, at rates of about an order of magnitude less. These higher order hydrocarbons were not seen in the Glycine Only control jars. This implies that the soil grains may provide sites where CH$_4$ is catalytically...
<table>
<thead>
<tr>
<th>Mars Jar</th>
<th>Designation</th>
<th>Production nmoles/hr</th>
<th>Flux $\mu$W/cm$^2$</th>
<th>$Q_{\text{CH}_4/\text{photon}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>High Flux</td>
<td>0.255</td>
<td>201</td>
<td>$1.49 \times 10^{-6}$</td>
</tr>
<tr>
<td>2</td>
<td>Low Flux</td>
<td>0.149</td>
<td>74.8</td>
<td>$2.89 \times 10^{-6}$</td>
</tr>
<tr>
<td>3</td>
<td>He Atmosphere</td>
<td>0.069</td>
<td>27.0</td>
<td>$4.94 \times 10^{-6}$</td>
</tr>
<tr>
<td>4</td>
<td>High Flux</td>
<td>0.205</td>
<td>155</td>
<td>$1.56 \times 10^{-6}$</td>
</tr>
<tr>
<td>5</td>
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<td>0.102</td>
<td>65.0</td>
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<td>6</td>
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<tr>
<td>7</td>
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<tr>
<td>8</td>
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<tr>
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<td>Glycine Only</td>
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Table 2.2: Mars Jars Quantum Efficiencies

transformed into higher molecular weight hydrocarbons. The Soil Only control jars also produced hydrocarbon gas upon irradiation, although not as much as in the Mars simulations. It is possible that unknown organic contaminants in the soil were also being destroyed. If this is true the CH$_4$ production in the Mars simulations may be interpreted to be due to the breakdown of the glycine plus unknown organics. The upper bound for the quantum efficiency may be considered to be the mean value plus one standard deviation,

$$Q_{\text{max}} = 2.56 \times 10^{-6} \text{ molecules/photon}$$

To consider the breakdown of glycine alone, the CH$_4$ production rate of the Soil Only control jars is subtracted from the CH$_4$ production rate of the Mars simulations. The lower bound for quantum efficiency may be taken to be the mean value minus one standard deviation, or $0.90 \times 10^{-6}$ molecules/photon. Subtracting the production rate of the Soil Only jar, a lower bound for the
quantum efficiency of glycine degradation may be calculated:

\[ Q_{\text{min}} = 0.54 \times 10^{-6} \text{ molecules/photon} \]

Once upper and lower bounds have been placed on laboratory measurements of glycine photodegradation, it is necessary to assess the impact these simulations have on the understanding of organic degradation on Mars. In general, more complex organic compounds, also found in carbonaceous meteorites, have UV absorptions at higher wavelengths (McLaren and Shugar 1964). Since these energies are more abundant in the solar radiation at the martian surface, higher degradation rates would apply. For example, Oro and Holtzer (1979) measured higher UV destruction rates for adenine and naphthalene than for glycine. The flux of 2000-2500 Å radiation at the surface is 2.57 \( \mu \)Watts cm\(^{-2} \) (Kuhn and Atreya 1979). With flux levels of 27 to 201 \( \mu \)Watts cm\(^{-2} \) from the Xe lamp, the Mars simulations provided UV fluxes that were 10 to 80 times those found at the martian surface. Scaling the experimental results to Mars, upper and lower bounds for organic degradation on Mars may be estimated to be

\[ D_{\text{min}} = 8.25 \times 10^{-4} \text{ g m}^{-2} \text{ yr}^{-1} \quad \text{and} \quad D_{\text{max}} = 2.85 \times 10^{-3} \text{ g m}^{-2} \text{ yr}^{-1} \]

for molecules with a molecular weight of about 100. This may be compared with the estimated flux of organic carbon to the surface via meteoritic infall. The rate was calculated based on meteoritic flux from Flynn and McKay (1989), and the assumption that 1% of the large fragments and 10% of the small ones is in the form of organic compounds. Upper and lower bounds for the influx are

\[ F_e = 6.9 \times 10^{-7} \text{ g m}^{-2} \text{ yr}^{-1} \quad \text{and} \quad F_e = 5.2 \times 10^{-5} \text{ g m}^{-2} \text{ yr}^{-1} \]
The laboratory simulations show scaled degradation rates that are at least 16 times higher than the meteoritic influx of carbon on Mars. If aeolean processes stir the loose layer of soil at the surface, much of the top layer will be exposed to the destructive UV radiation. The conclusion, based upon laboratory simulations, is that UV radiation alone may well be responsible for eliminating organic compounds at the surface of Mars.
Figure 2.1: Mars Jar
Figure 2.2: Mars Jars Gas Manifold

Figure 2.3: Mars Jars Experimental Apparatus
Figure 2.4: Mars Jars Sample Bulb

Figure 2.5: Perkin Elmer 900 Gas Chromatograph
Figure 2.6  UV Detector Calibration Curve
Xe Lamp Flux Distribution 2000 - 2500 A
\[\mu\text{Watts/cm}^2\]

Mars Jars Placement

Figure 2.9: Xe Lamp Flux Distribution

24
RUN # 53

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TOTAL AREA = 3.9000E+07
MUL FACTOR = 1.6000E+00

Figure 2.10: GC Hydrocarbon Standards Chromatogram
Figure 2.11: GC Sample Chromatogram
Figure 2.13  Hydrocarbon Production—Low Flux Jar #2

Hydrocarbon Quantity (nanomoles)

Methane  Ethane  Ethylene

Time (hours)
Figure 2.14  Hydrocarbon Production—He Atmosphere Jar #3
Figure 2.15  Hydrocarbon Production—High Flux Jar #4
Figure 2.16  Hydrocarbon Production—He Atmosphere Jar #5
Figure 2.17 Hydrocarbon Production—Soil Only Jar #6

Hydrocarbon Quantity (nanomoles) vs. Time (hours)
Figure 2.18 Hydrocarbon Production—High Flux Jar #7
Figure 2.19  Hydrocarbon Production—Low Flux Jar #8
Figure 2.20  Hydrocarbon Production—Glycine Only Jar #9

Hydrocarbon Quantity (nanomoles) vs. Time (hours)

- Methane
- Ethane
- Ethylene
Figure 2.21  Hydrocarbon Production—Darkness Control Jar #10
Figure 2.22: The Glycine Molecule
Figure 2.23  Mars Jars Quantum Efficiencies
Figure 2.24  Quantum Efficiency Histogram
<table>
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<th>HYDROCARBON STANDARDS</th>
<th>PERKIN ELMER 900</th>
<th>8/19/90</th>
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<tr>
<td>PORASIL C COLUMN</td>
<td>STANDARD C</td>
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| INJECTIONS          | 13,14,15,16     | Ntotal (nmoles): 11057.49 |
| INITIAL PRESSURE    | 759             | TEMPERATURE (K): 295       |
| VOLUME RATIO:       | 0.988           | INJECTION VOLUME (cc): 0.268 |

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<th>s(%)</th>
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Table 2.3: GC Hydrocarbon Standards Spreadsheet
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<th>Acorr (counts)</th>
<th>ns (nmole/cm)</th>
<th>Nm (nmole)</th>
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<th>Nprod (nmole)</th>
<th>Ntot prod (nmole)</th>
<th>N/hr</th>
<th>FLUX (nmole/h/watts/cm²)</th>
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<td>73</td>
<td>1.04E+16</td>
<td>1.23E-06</td>
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</tbody>
</table>

| AVERAGE | 0.124 | 117.29 | 1.67E+16 | 1.27E-06 |
| STD. DEVIATION | 0.073 | 24.27 | 3.45E+15 | 6.78E-07 |

Table 2.4: Mars Jars Data Analysis Spreadsheet
Chapter 3

Hydrogen Peroxide Transport on Mars

3.1 Introduction

The results of the laboratory investigations reported in the previous chapter indicate that the lack of organics found by the Viking GCMS may be due entirely to the intense solar UV flux at the martian surface. However, other Viking Lander experiments, such as the Labeled Release (LR) and Gas Exchange (GEX) experiments also indicated that the soil itself is oxidizing (Klein 1978). The oxidizing agents may also be responsible for the degradation of organics, particularly at depths that are never exposed to UV radiation. Although there is a wide variety of explanations for the oxidizing nature of the martian soil, it has been shown through laboratory experiments (Oyama and Berdahl 1979) that $\text{H}_2\text{O}_2$ in Mars analog soils closely mimics the kinetics of the $\text{CO}_2$ evolution in
the LR experiment. Additionally, it is known that $H_2O_2$ exists in the martian atmosphere (Kong and McElroy 1977), and may be deposited on the surface (Hunten 1979). The thermal sensitivity of the LR experiment is also consistent with a thermally labile oxidant, such as $H_2O_2$. The large amounts of $O_2$ evolved in the GEX may be harder to explain. Although alkali and alkaline earth peroxides may be responsible (Oyama et al. 1976), it has been postulated that $O_2$ is adsorbed onto soil grains near the surface (Fanale et al. 1982). As a working model for the oxides in the martian soil, it is assumed that adsorbed $O_2$ is responsible for the GEX results, and $H_2O_2$ is responsible for the evolution of $CO_2$ in the LR experiment. Although additional oxides near the surface may be responsible for the GEX results, $H_2O_2$ may have the opportunity to diffuse to significant depths because of its atmospheric reservoir. It is natural to ask at what depths $H_2O_2$ may exist in the martian soil. Although it must certainly diffuse downwards, $H_2O_2$ will also be adsorbed onto soil grains. $H_2O_2$ is also known to be unstable in the presence of iron (Schumb 1955), and will be catalytically destroyed at some rate. If the concentration of $H_2O_2$ becomes very small at some depth, it is possible that organics may still survive beneath this oxidizing layer.

This chapter reports on a series of theoretical models that seek to determine the distribution of $H_2O_2$ in the martian environment. In each of the next four sections, martian $H_2O_2$ transport models of increasing complexity are developed. As an initial consideration, a simple linear diffusion model of $H_2O_2$ in the martian soil is described. The boundary condition at the soil/atmosphere interface is considered to be either a given concentration of adsorbed $H_2O_2$ or a known flux into the soil surface. Since the partitioning between two phases of $H_2O_2$ in
the soil is a key feature of these transport models, it is introduced in the simplest possible way in this first model. The ratio of adsorbed to vapor phase \( \text{H}_2\text{O}_2 \) is taken to be constant at all depths. The next model treats the partitioning between \( \text{H}_2\text{O}_2 \) phases in a more sophisticated way. Isotherms for water under martian conditions, empirically determined by Fanale and Cannon (1971) are adopted to describe the adsorption of \( \text{H}_2\text{O}_2 \) on martian soil grains. This analytical form for the phase partitioning yields a nonlinear diffusion equation which is solved with boundary conditions analogous to the first model's. The next level of sophistication is developed in the third model. Here, the photochemical production and loss of \( \text{H}_2\text{O}_2 \) in the atmosphere is considered, and a mass balance equation for the atmosphere is coupled with the soil diffusion equation. Thermal motion of \( \text{H}_2\text{O}_2 \) in the atmosphere and soil pore spaces allows molecules to be transported through the soil/atmosphere interface. The net flux of \( \text{H}_2\text{O}_2 \) across the boundary is driven by the gradient set up in the soil by diffusion and loss mechanisms. For this model, there is a return to the simplified scheme for phase partitioning—the linear soil diffusion equation is once again considered. The culmination of the modeling process is achieved in the fourth model, where a fully coupled soil/atmosphere system is considered, along with a soil diffusion equation that incorporates the nonlinear adsorption isotherms. It is only in this model that the physics of the process are considered entirely, without resort to \textit{ad hoc} assumptions. The Table 3.1 suggests a way to organize these four models. The relevant differences fall into two categories—linear or nonlinear models, and uncoupled or coupled models.
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<th>Coupled Soil/Atmosphere Models</th>
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<td><strong>Linear</strong></td>
<td>Section 3.2 Linear Soil Diffusion Model</td>
<td>Section 3.4 Coupled Soil/Atmosphere Model</td>
</tr>
<tr>
<td><strong>Nonlinear</strong></td>
<td>Section 3.3 Nonlinear Soil Diffusion Model</td>
<td>Section 3.5 Nonlinear Coupled Soil Atmosphere Model</td>
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</table>

Table 3.1: Hydrogen Peroxide Transport Models
3.2 Linear Soil Diffusion Model

In order to understand the distribution of $\text{H}_2\text{O}_2$ in the martian soil, a simple model based upon the diffusion of $\text{H}_2\text{O}_2$ through a permeable soil is developed. It is assumed that $\text{H}_2\text{O}_2$ produced in the martian atmosphere is in some way transferred to the soil surface. The $\text{H}_2\text{O}_2$ then diffuses downwards. It is further assumed that some fraction of the $\text{H}_2\text{O}_2$ is adsorbed onto the soil grains, and that the adsorbed $\text{H}_2\text{O}_2$ undergoes heterogenous catalytic destruction. The ratio of vapor phase to adsorbed phase $\text{H}_2\text{O}_2$, $f$, is assumed to be constant. This constant is derived from isotherms determined by Fanale and Cannon (1971) for water under martian conditions. The linear phase partitioning is adopted in order to keep the soil diffusion equation linear, and therefore easier to solve. More realistic phase partitioning functions may be incorporated into future models. The catalytic destruction is characterized by a lifetime, $\tau$, against catalytic destruction. This first order model ignores the question of how $\text{H}_2\text{O}_2$ is deposited onto the surface from the atmosphere. The two cases discussed are:

1. **Density Case** – The adsorbed phase concentration is taken to be that inferred from the Viking LR experiment, 30 nmoles cm$^{-3}$ (Klein 1978). The lifetime of $\text{H}_2\text{O}_2$ in the soil is taken to be that inferred by Chyba et al. (1989), also from the Viking LR experiment. It is $10^5$ years, or $3.15 \times 10^{12}$ seconds.

2. **Flux Case** – The flux into the soil is taken to be identical with the odd hydrogen production rate (Hunten 1979), $4 \times 10^9$ cm$^{-2}$ sec$^{-1}$. The lifetime of $\text{H}_2\text{O}_2$ in this case is assumed to be one terrestrial year, or $3.15 \times 10^7$
seconds.

3.2.1 Phase Partitioning

At martian temperatures and pressures, $\text{H}_2\text{O}_2$ will exist in both a condensed and vapor phase. It is assumed that the condensed phase is in the form of molecules physically adsorbed onto the soil grains, and that it is only these molecules that are available for catalytic destruction. Vapor phase molecules in the soil pore spaces are available for downward diffusion. Although the relative concentration of the vapor and adsorbed phases is a complex function of temperature, pressure and absolute concentrations, the simple assumption is made here that this quantity is a constant. The value of this constant is determined from empirical work done by Fanale and Cannon (1971) on the adsorption of water under martian conditions. The data was taken for the adsorption of $\text{H}_2\text{O}$ onto clean basalt surfaces for concentrations several orders of magnitude higher than those expected for $\text{H}_2\text{O}_2$ adsorbed onto martian soil grains. Nevertheless, since $\text{H}_2\text{O}_2$ has a dipole moment and vapor pressure curve similar to $\text{H}_2\text{O}$, the Fanale and Cannon isotherms will be used as a starting point to estimate $\text{H}_2\text{O}_2$ phase partitioning under martian conditions. The adsorption data are represented by an expression that gives the number of grams of $\text{H}_2\text{O}_2$ adsorbed per gram of soil, as a function of temperature and partial pressure. The expression is

$$R_a = \gamma P^{0.51} e^{-\frac{f}{T}}$$

where:

$R_a$ = grams of adsorbed $\text{H}_2\text{O}_2$ per gram of soil
\[ P = \text{partial pressure of } H_2O_2 \]

\[ T = \text{temperature (in Kelvins)} \]

and the empirically derived coefficients are:

\[ \gamma = \frac{A_o}{C_o B_o} \quad \text{and} \quad \delta = B_o D_o \]

where:

\[ A_o = 11.364 \times 10^{-3} \]

\[ B_o = 0.51 \]

\[ C_o = 1.84 \times 10^{12} \mu \text{bar} \]

\[ D_o = -5254.5 \text{ K} \]

The expression must be converted to obtain the number density of adsorbed \( H_2O_2 \) in terms of the number density of vapor phase \( H_2O_2 \) in the soil pore spaces.

\[ R_a = \frac{g_{H_2O_2}}{g_{soil}} = \frac{\rho_{H_2O_2}}{\rho_{soil}} \]

where \( g_{H_2O_2} \) and \( g_{soil} \) are the masses of adsorbed \( H_2O_2 \) and soil, respectively. Also, \( \rho_{H_2O_2} \) and \( \rho_{soil} \) are the densities of the adsorbed \( H_2O_2 \) and soil, respectively.

If \( \mu \) is the molecular weight of \( H_2O_2 \), \( N_o \) is Avagadro’s number, and \( n_c \) is the concentration of adsorbed \( H_2O_2 \),

\[ \frac{\rho_{H_2O_2}}{\rho_{soil}} = \frac{n_c \mu_{H_2O_2}}{N_o \rho_{soil}} \]

Using the ideal gas law, if \( n_v \) is the concentration of vapor phase \( H_2O_2 \) in the soil pore spaces, the pressure is

\[ P = \frac{n_v}{N_o} RT \]

48
\[
\frac{n_c \mu_{H_2O_2}}{N_o \rho_{soil}} = \frac{A_o}{C_o^{0.51}} \left( \frac{n_v}{N_o} \frac{RT}{N_o} \right)^{0.51} e^{-\frac{E_a}{T}} \\
n_c = \left[ \frac{\rho_{soil} A_o N_o}{C_o^{0.51} \mu_{H_2O_2}} \left( \frac{RT}{N_o} \right)^{0.51} e^{-\frac{E_a}{T}} \right] n_v^{0.51}
\]

For inclusion of this expression in the analytical model, the exponent is approximated by 0.5. Then the phase partitioning function is

\[
n_c(z) = S(T)n_v^{\frac{1}{2}}(z)
\]  

(3.1)

where:

\[
S(T) = \frac{\rho_{soil} A_o N_o}{C_o^{0.51} \mu_{H_2O_2}} \left( \frac{RT}{N_o} \right)^{0.51} e^{-\frac{E_a}{T}}
\]

For this isothermal model, an average martian surface temperature of 215 K is used. Isotherms for several temperatures are shown if Figure 3.1. For the model, S is calculated using the following values:

\[
\rho_{soil} = 1.3 \text{ g cm}^{-3}
\]

\[
N_o = 6.02 \times 10^{23} \text{ mole}^{-1}
\]

\[
\mu_{H_2O_2} = 34 \text{ g mole}^{-1}
\]

\[
R = 0.0823 \text{ litre atm mole}^{-1} \text{ K}^{-1}
\]

\[
T = 215 \text{ K}
\]

\[
S(215) = 4.737 \times 10^{12} \text{ cm}^{-\frac{3}{2}}
\]

For the sake of analytical simplicity, the full functional form for the phase partitioning, Equation 3.1 will not be used. Instead, an average over adsorbed concentrations from 0 to 30 nmoles cm\(^{-3}\) is calculated. This yields an approximate (constant) number for the ratio of vapor phase to adsorbed phase H\(_2\)O\(_2\).
The number calculated with these simplifying assumptions is

\[ f = 8 \times 10^{-10} \]

### 3.2.2 The Model

The rate of change of vapor phase H\textsubscript{2}O\textsubscript{2} in a volume cell depends upon the porosity of the soil, \( \varepsilon \). This is the ratio of the interstitial pore space volume to total volume. The catalytic destruction of H\textsubscript{2}O\textsubscript{2} is characterized by its lifetime in the soil, \( \tau \). If \( D \), then, is the diffusion coefficient for H\textsubscript{2}O\textsubscript{2}, the diffusion equation is

\[ \varepsilon \frac{\partial n_v(z,t)}{\partial t} + \frac{\partial n_c(z,t)}{\partial t} = Df \frac{\partial^2 n_c(z,t)}{\partial z^2} - \frac{n_c(z,t)}{\tau} \]  

(3.2)

where \( n_c(z,t) \) is the concentration of adsorbed H\textsubscript{2}O\textsubscript{2} and \( n_v(z,t) \) is the concentration of vapor phase H\textsubscript{2}O\textsubscript{2} in the soil pore spaces. Considering the limit to steady state,

\[ \lim_{t \to \infty} \frac{\partial n_c(z,t)}{\partial t} = 0 \quad \text{and} \quad \lim_{t \to \infty} n_c(z,t) = n_c(z) \]

The steady state soil equation is:

\[ \frac{\partial^2 n_c(z)}{\partial z^2} - \frac{1}{D\tau f} n_c(z) = 0 \]  

(3.3)

### Density Case

The boundary conditions for this case are:

**BC 1**

\[ \lim_{z \to \infty} n_c(z) = 0 \]
BC 2

\[ n_c(0) = 30 \text{ nmoles cm}^{-3} \]

Solutions have the form

\[ n_c(z) = Ae^{z/\sqrt{D\tau f}} + Be^{-z/\sqrt{D\tau f}} \]

Applying BC 1,

\[ \lim_{z \to \infty} n_c(z) = 0 \]

so that \( B = 0 \). Applying BC 2, it is seen that

\[ A = n_c(0) \]

The solution is therefore

\[ n_c(z) = n_c(0)e^{-z/\sqrt{D\tau f}} \quad (3.4) \]

with a \( \frac{1}{3} \) folding depth of

\[ \delta = \sqrt{D\tau f} \quad (3.5) \]

Flux Case

The boundary conditions for this case are:

BC 1

\[ \lim_{z \to \infty} n_c(z) = 0 \]

which is the same as for the Density Case, and

BC 2

\[ -D \frac{\partial n_v(z)}{\partial z} \bigg|_{z=0} = F_i \]
where \( F_i \) is the flux of \( \text{H}_2\text{O}_2 \) into the soil. It is taken here to be equal to the odd hydrogen column production rate in the atmosphere. Applying BC 1 as before, the same solution is obtained,

\[
n_c(z) = n_c(0)e^{-z/\sqrt{D\tau f}}
\]

Applying BC 2, the phase partitioning function is used to write the boundary condition in terms of \( n_c(z) \),

\[
-Df \left. \frac{\partial n_c(z)}{\partial z} \right|_{z=0} = F_i
\]

\[
\frac{Df n_c(0)}{(D\tau f)^{\frac{1}{2}}} = F_i
\]

So that the expression for the surface concentration in terms of the flux into the soil is:

\[
n_c(0) = \frac{F_i}{f} \left( \frac{\tau f}{D} \right)^{\frac{1}{2}}
\]

and the \( \frac{1}{e} \) folding depth is still:

\[
\delta = \sqrt{D\tau f}
\]

### 3.2.3 Results

**Density Case**

The following values are used in the Density Case calculations:

\[
D = 0.0163 \text{ cm}^2 \text{ sec}^{-1}
\]

\[
\tau = 3.15 \times 10^{12} \text{ sec}
\]

\[
f = 8 \times 10^{-10}
\]
\[ n_e(0) = 30 \text{ nmoles cm}^{-3} \]

Using these values, the \( \frac{1}{e} \) folding depth is:

\[ \delta = 6.401 \text{ cm} \]

\( \text{H}_2\text{O}_2 \) concentration vs. depth for the Density Case is plotted in Figure 3.2.

**Flux Case**

The following values are used in the Flux Case calculations:

\[ D = 0.0163 \text{ cm}^2 \text{ sec}^{-1} \]
\[ \tau = 3.15 \times 10^7 \text{ sec} \]
\[ f = 8 \times 10^{-10} \]
\[ F_i = 4 \times 10^9 \text{ cm}^{-2} \text{ sec}^{-1} \]

For the Flux Case, the surface concentration is:

\[ n_e(0) = 10,324 \text{ nmoles cm}^{-3} \]

and the \( \frac{1}{e} \) folding depth is:

\[ \delta = 0.02 \text{ cm} \]

\( \text{H}_2\text{O}_2 \) concentration vs. depth for the Flux Case is plotted in Figure 3.3. The lifetime of \( \text{H}_2\text{O}_2 \) under martian surface conditions is poorly constrained. Therefore, the values used in these two cases are somewhat arbitrary. In order to investigate the behavior of the model for a wide range of lifetimes, the \( \frac{1}{e} \) folding depth is plotted vs. lifetime in Figure 3.4.
3.2.4 Discussion

The model requires that both the top boundary condition and the lifetime of H$_2$O$_2$ in the soil be specified. A density boundary condition and a lifetime are inferred from the Viking Lander data in the Density Case. The $\frac{1}{e}$ depth for H$_2$O$_2$ concentration is found to be quite shallow – about 6.4 cm. In the Flux Case, the boundary condition is the flux into the soil, and is taken to be the entire H$_2$O$_2$ column production rate in the atmosphere. The lifetime for this case was arbitrarily chosen to be one terrestrial year. The resulting surface concentration is much higher than for the Density Case (10,300 nmoles cm$^{-3}$ versus 30 nmoles cm$^{-3}$) due to the high flux into the soil. The $\frac{1}{e}$ depth is even more shallow due to the shorter lifetime of H$_2$O$_2$ in the soil.
Figure 3.1
H$_2$O$_2$ Adsorption Isotherms

Vapor Phase H$_2$O$_2$ (molecules cm$^{-3}$)

$\frac{n_v}{n_c} = 8 \times 10^{-6}$

$T = 205$ K
$T = 215$ K
$T = 225$ K

adsorbed H$_2$O$_2$ (nmole cm$^{-2}$)
Figure 3.2  Density Case -- Linear Soil Diffusion Model

$H_2O_2$ Depth Profile

Concentration (mnoles cm$^{-3}$)

Depth (cm)
Figure 3.3  
Flux Case — Linear Soil Diffusion Model

H₂O₂ Depth Profile

Concentration (nmole/cm²) vs Depth (cm)
Figure 3.4  Depth vs. Lifetime — Linear Soil Diffusion Model
3.3 Nonlinear Soil Diffusion Model

The first step in making the simple diffusion model of the last section more sophisticated is to incorporate a more realistic phase partitioning between the adsorbed and vapor phases. In the linear diffusion model it was assumed that the two phases exist in constant proportion for all concentrations, and therefore for all depths. In the following enhancement to the soil diffusion model, the empirically determined isotherms for water under martian conditions (Fanale and Cannon 1971) are adapted for the purpose of more accurate partitioning of the H$_2$O$_2$ phases. In general, this leads to a diffusion equation that is nonlinear. Again, two cases are considered.

1. **Density Case** – The adsorbed phase H$_2$O$_2$ concentration at the surface is assumed to be that inferred from the Viking LR experiment results. The half-life against catalytic destruction for the H$_2$O$_2$ is taken to be the number estimated by Chyba et al. (1989). The parameters used are:

   \[ n_c(0) = 30 \text{ nmoles cm}^{-3} \]
   \[ \tau = 3.15 \times 10^{12} \text{ sec} \]

2. **Flux Case** – Flux into the soil is assumed to be one half the atmospheric column production rate of odd hydrogen species (Hunten 1979). The half-life against catalytic destruction of the H$_2$O$_2$ is arbitrarily taken to be one year. The parameters used are:

   \[ F_i = 2 \times 10^9 \text{ cm}^{-2} \text{ sec}^{-1} \]
   \[ \tau = 3.15 \times 10^7 \text{ sec} \]
3.3.1 Soil Diffusion Model

The soil diffusion equation is the same one that has been considered previously:

\[
\frac{\partial n_v(z,t)}{\partial t} + \frac{\partial n_c(z,t)}{\partial t} = D \frac{\partial^2 n_v(z,t)}{\partial z^2} - \frac{n_c(z,t)}{\tau}
\]

With boundary conditions:

**BC 1**

\[
\lim_{z \to \text{large}} \frac{\partial n_v(z,t)}{\partial z} = 0
\]

**BC 2 Density Case**

\[n_c(0) = 30 \text{ nmoles cm}^{-3}\]

**BC 2 Flux Case**

\[-D \left. \frac{\partial n_v(z,t)}{\partial z} \right|_{z=0} = F_i\]

The soil diffusion equation is to be solved for the steady state,

\[
\lim_{t \to \infty} \frac{\partial n_c(z,t)}{\partial t} = 0 \quad \text{and} \quad \lim_{t \to \infty} n_c(z,t) = n_c(z)
\]

The steady state soil diffusion equation is then

\[
\frac{d^2 n_v(z)}{dz^2} - \frac{n_c(z)}{D \tau} = 0
\]  \hspace{1cm} (3.6)

Next, the phase partitioning function, derived in section 3.2.1 is again introduced (Equation 3.1).

\[n_c(z) = S(T)n_v^{\frac{1}{2}}(z)\]

and the isothermal soil diffusion equation becomes

\[
\frac{d^2 n_v(z)}{dz^2} = \frac{S}{D \tau}n_v^{\frac{1}{2}}(z)
\]  \hspace{1cm} (3.7)

which may be integrated once to obtain

\[
\frac{dn_v}{dz} = \pm \left[ \frac{4S}{3D \tau} n_v^{\frac{3}{2}} + C_1 \right]^{\frac{1}{2}}
\]
Applying BC 1,
At some depth, \( n_v \rightarrow 0 \). At this depth, it is also expected that \( \frac{dn_v}{dz} \rightarrow 0 \).
Therefore, for any physical solution, \( C_1 = 0 \). On physical grounds, it is expected that the concentration of \( \text{H}_2\text{O}_2 \) will decrease with depth, therefore \( \frac{dn_v}{dz} < 0 \).

\[
\frac{dn_v}{dz} = -\frac{2}{\sqrt{3}} \left( \frac{S}{D\tau} \right)^{\frac{1}{2}} n_v^{\frac{3}{2}}
\]

Integrating again,

\[
n_v(z) = \left[ C_2 - \frac{1}{2\sqrt{3}} \left( \frac{S}{D\tau} \right)^{\frac{1}{2}} z \right]^4
\]

Since

\[
n_c(z) = Sn_v^\frac{1}{2}(z)
\]

the adsorbed phase concentration is

\[
n_c(z) = \left[ S^{\frac{1}{2}} C_2 - \frac{1}{2\sqrt{3}} \left( \frac{S}{D\tau} \right)^{\frac{1}{2}} z \right]^2
\]

Applying BC 2 – Density Case
At \( z = 0 \),

\[
n_c(0) = SC_2^2
\]

\[
C_2 = \frac{n_v^\frac{1}{2}(0)}{S^\frac{1}{2}}
\]

So the solution to the soil diffusion equation for the Density Case is

\[
n_c(z) = \left[ n_v^\frac{1}{2}(0) - \frac{1}{2\sqrt{3}} \left( \frac{S}{D\tau} \right)^{\frac{1}{2}} z \right]^2
\]

(3.8)

Applying BC 2 – Flux Case

\[
\frac{dn_v}{dz} = 4 \left[ C_2 - \frac{1}{2\sqrt{3}} \left( \frac{S}{D\tau} \right)^{\frac{1}{2}} z \right]^3 \left[ -\frac{1}{2\sqrt{3}} \left( \frac{S}{D\tau} \right)^{\frac{1}{2}} \right]
\]

\[
-D \frac{dn_v}{dz} \bigg|_{z=0} = 4C_2^3D \frac{1}{2\sqrt{3}} \left( \frac{S}{D\tau} \right)^{\frac{1}{2}} = F_i
\]
\[ C_2 = \left( \frac{F_i}{2} \right)^{\frac{1}{2}} \left( \frac{3\tau}{DS} \right)^{\frac{1}{2}} \]

So the solution to the soil diffusion equation for the Flux Case is,

\[ n_c(z) = \left[ \left( \frac{SF_i}{2} \right)^{\frac{1}{2}} \left( \frac{3\tau}{D} \right)^{\frac{1}{2}} - \frac{1}{2\sqrt{3}(D\tau)^{\frac{1}{2}}} \right]^2 \] (3.9)

Note that by comparing the first terms in the solutions to the density and flux cases, an expression for the flux into the soil may be derived in terms of the surface H$_2$O$_2$ concentration and destruction and diffusion parameters,

\[ F_i = \frac{2}{S} \left( \frac{D}{3\tau} \right)^{\frac{1}{2}} n_c^2(0) \] (3.10)

or, the surface concentration may be expressed in terms of the flux of H$_2$O$_2$ into the soil and destruction and diffusion parameters,

\[ n_c(0) = \left( \frac{SF_i}{2} \right)^{\frac{1}{2}} \left( \frac{3\tau}{D} \right)^{\frac{1}{2}} \] (3.11)

### 3.3.2 Numerical Results

**Density Case**

For the Density Case, the adsorbed H$_2$O$_2$ concentration is constrained, and the solution to the soil diffusion equation is given by Equation 3.8,

\[ n_c(z) = \left[ n_c^2(0) - \frac{1}{2\sqrt{3}(D\tau)^{\frac{1}{2}}} \right]^2 \]

The concentration of adsorbed H$_2$O$_2$ goes to zero at a finite depth, \( z_e \), where

\[ z_e = \frac{2\sqrt{3}}{S} (D\tau)^{\frac{1}{2}} n_c^{\frac{1}{2}}(0) \]
Using the following values for the calculations,

\[ n_e(0) = 30 \text{ nmoles cm}^{-3} \]
\[ D = 0.0163 \text{ cm}^{-2} \text{ sec}^{-1} \]
\[ \tau = 3.15 \times 10^{12} \text{ sec}^{-1} \]
\[ S = 4.737 \times 10^{12} \text{ cm}^{-\frac{3}{2}} \]

the extinction depth is calculated to be:

\[ z_e = 22.246 \text{ cm} \]

The flux of H$_2$O$_2$ into the soil necessary to sustain this surface concentration is given by Equation 3.10 and is

\[ F_i = 4.253 \times 10^{4} \text{ cm}^{-2} \text{ sec}^{-1} \]

or about 5 orders of magnitude lower than the atmospheric column production rate.

**Flux Case**

For the case where the flux of H$_2$O$_2$ into the soil is given, the solution to the soil diffusion equation is given by Equation 3.9,

\[ n_e(z) = \left[ \left( \frac{SF_i}{2} \right)^{\frac{1}{3}} \left( \frac{3\tau}{D} \right)^{\frac{1}{2}} - \frac{1}{2\sqrt{3}} \frac{S}{(D\tau)^{\frac{1}{2}}} \right]^2 \]

The concentration of adsorbed H$_2$O$_2$ goes to zero at a finite depth, \( z_e \), given by:

\[ z_e = \left( \frac{36F_iD\tau^2}{S^2} \right)^{\frac{1}{3}} \]
The following values are used for the calculations:

\[ S = 4.737 \times 10^{12} \text{ cm}^{-\frac{3}{2}} \]
\[ F_i = 2 \times 10^9 \text{ cm}^{-2} \text{ sec}^{-1} \]
\[ \tau = 3.15 \times 10^7 \text{ sec} \]
\[ D = 0.0163 \text{ cm}^2 \text{ sec}^{-1} \]

The extinction depth is:

\[ z_e = 0.3727 \text{ cm} \]

Under these conditions, the concentration of adsorbed \( \text{H}_2\text{O}_2 \) at the surface will be given by Equation 3.11, and will be:

\[ n_c(0) = 842.075 \text{ nmoles cm}^{-3} \]

which is an order of magnitude larger than the Viking LR experiment results.

### 3.3.3 Discussion

The model predicts an extinction depth, beyond which there can be no \( \text{H}_2\text{O}_2 \) at all. This is caused by the nonlinear nature of the soil diffusion equation. The greater the depth, the less vapor phase \( \text{H}_2\text{O}_2 \) there is, and the less vapor phase \( \text{H}_2\text{O}_2 \) there is, the more adsorbed phase \( \text{H}_2\text{O}_2 \) there is in proportion to it. Since there is a higher proportion of adsorbed \( \text{H}_2\text{O}_2 \) at greater depth, there is more \( \text{H}_2\text{O}_2 \) available, proportionally, to be destroyed. This results in a positive feedback that destroys \( \text{H}_2\text{O}_2 \) rapidly and results in complete extinction at a definite depth. In particular, the Density Case shows that if the model is constrained to be consistent with the Viking LR experiment results, the extinction depth for
H$_2$O$_2$ is quite shallow, being only 22 cm. For this case, the flux into the soil is many orders of magnitude smaller than the atmospheric odd hydrogen column production rate. If instead the model is constrained so that H$_2$O$_2$ enters the soil at the same rate it is produced in the atmosphere, the extinction depth for H$_2$O$_2$ is even smaller, 0.4 cm, and the surface concentration of H$_2$O$_2$ is roughly only an order of magnitude higher than that assumed for the Density Case.
Figure 3.5  Density Case — Nonlinear Soil Diffusion Model
Figure 3.6
Flux Case — Nonlinear Soil Diffusion Model
3.4 Coupled Soil/Atmosphere Model

In an effort to eliminate the *ad hoc* introduction of \( \text{H}_2\text{O}_2 \) into the soil, in this section a simple model that couples the creation, transport and destruction of \( \text{H}_2\text{O}_2 \) in the atmosphere with its transport and destruction in the soil is developed. Photochemical models of the martian atmosphere that neglect losses to the soil predict concentrations of about \( 2 \times 10^9 \text{ cm}^{-3} \) (Kong and McElroy 1977). Based upon the thermal motion of \( \text{H}_2\text{O}_2 \) molecules at a martian surface temperature of 215 K, this represents a flux into the soil of about \( 3 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1} \). However, total atmospheric column production rates have been calculated to be about \( 4 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1} \), which has been used as an estimate for the total flux into the soil (Hunten 1987). By considering the diffusion and catalytic destruction of \( \text{H}_2\text{O}_2 \) in the soil, coupled expressions for atmospheric and soil concentrations are derived. The solution to the soil diffusion equation yields concentration as a function of depth, and a \( \frac{1}{e} \) folding depth. Flux into the soil is due to the thermal motion of \( \text{H}_2\text{O}_2 \), and is driven by a gradient that is due to diffusion and destruction mechanisms in the soil. In the model presented here, the following assumptions are made:

1. \( \text{H}_2\text{O}_2 \) is created in the atmosphere at a column production rate of \( 4 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1} \).

2. Losses in the martian atmosphere due to photodissociation are characterized by a decay constant of \( 2.5 \times 10^{-5} \text{ s}^{-1} \). (Parkinson and Hunten 1972)
3. H$_2$O$_2$ is deposited into the soil by the thermal motion of molecules at the surface.

4. H$_2$O$_2$ exists in the soil in a condensed phase. For the purposes of this model, the simple assumption is made that the majority of H$_2$O$_2$ is physically adsorbed on the surface of the soil grains, and that vapor phase H$_2$O$_2$ exists in the pore spaces in equilibrium with the adsorbed phase. This equilibrium is expressed as a simple ratio between the vapor phase and adsorbed phase concentrations,

$$f = \frac{n_v(z)}{n_c(z)}$$

where $n_v(z)$ is the vapor phase number density of H$_2$O$_2$ and $n_c(z)$ is the adsorbed phase number density of H$_2$O$_2$. This treatment of the phase partitioning is the same as in section 3.2.

5. The transport of H$_2$O$_2$ through the soil is accomplished by diffusion of the vapor phase. At a Mars average temperature of 215 K and surface pressure of 6 mbars, the mean free path of H$_2$O$_2$ is about 28 μm. Since the average pore size of the martian regolith is considerably smaller than this, about 1 μm (Fanale et al. 1986), diffusion is dominated by collisions with grain surfaces. This process is known as Knudsen diffusion. The diffusion coefficient is given as $D_K = \frac{4}{9} \frac{r e^2}{\pi^2} \left[ \frac{2kT}{m} \right]$, and has a value under these conditions of $D_K = 0.0163$ cm$^{-2}$ sec$^{-1}$.

6. Since vapor phase H$_2$O$_2$ at the surface of the soil is free to reenter the atmosphere, the assumption is made that the thermal motion of H$_2$O$_2$ molecules at the surface is responsible for a flux of molecules back into the atmosphere.
7. Adsorbed $H_2O_2$ in the soil undergoes decomposition to water at some rate characterized by a lifetime, $\tau$. The proposed mechanism is heterogenous catalysis on iron rich soil grains (Schumb 1955). As a result of the diffusion and catalytic destruction of $H_2O_2$ in the soil, and of the replenishment of $H_2O_2$ from the atmosphere, a depth profile for the concentration of $H_2O_2$ in the martian soil may be calculated.

In analyzing the solutions to the model two approaches are considered:

1. **Density Case** - The lifetime of $H_2O_2$ in the soil is unconstrained. The average concentration of $H_2O_2$ in the top 4 cm (Klein et al. 1976) is inferred from the Viking Labeled Release experiment. The assumption is made that $H_2O_2$ in the martian soil is responsible for the release of $CO_2$ in the LR experiment. The average surface concentration necessary to explain the LR results is about 30 nmoles cm$^{-3}$ (Klein 1978).

2. ** Lifetime Case** - The soil surface concentration of the $H_2O_2$ is unconstrained. In this case, experimental data for the lifetime of $H_2O_2$ in the soil is employed. A lifetime calculated by Chyba et al. (1989) based upon inferred activation energies from the Viking Labeled Release experiment is used. This lifetime is about $3.15 \times 10^{12}$ sec.
3.4.1 The Model

The model is comprised of two coupled partial differential equations. The first order atmosphere equation,

$$\frac{dN_a(t)}{dt} = P - lN_a(t) - F_i + F_o \quad (3.12)$$

is a simple conservation equation for the column number density, where:

- $N_a(t)$ is the column number density of H$_2$O$_2$ molecules
- $P$ is the column production rate
- $l$ is the loss rate of H$_2$O$_2$ in the atmosphere
- $F_i$ is the flux into the soil
- $F_o$ is the flux out of the soil

For an isothermal atmosphere with an exponential lapse rate,

$$n_a(z) = n_a(0)e^{-\frac{z}{H}}$$

where:

- $n_a(z)$ is the number density as a function of altitude
- $H$ is the density scale height

The number density of the atmosphere at the surface is given by

$$n_a(0) = \frac{N_a}{H}$$

The flux into the soil is assumed to be the rate at which molecules impinge upon the surface due to thermal motion.

$$F_i = \frac{1}{4}cn_a(0)$$
where:
\[
c = \sqrt{\frac{8kT}{\pi m}} , \text{ the average molecular speed at 215 K.}
\]

At martian surface temperatures, H$_2$O$_2$ is expected to exist in both adsorbed and vapor phases. Since only the vapor phase is mobile, it is the vapor phase concentration that contributes to a flux of H$_2$O$_2$ out of the soil and into the atmosphere column. The concentration of adsorbed phase H$_2$O$_2$ is denoted as $n_c(z)$, and the number density of the vapor phase is $n_v(z)$. Then the flux of H$_2$O$_2$ out of the soil and into the atmosphere column is:
\[
F_o = \frac{1}{4}cn_v(0)
\]
or, using the phase partitioning factor,
\[
F_o = \frac{1}{4}cfn_c(0)
\]
The conservation equation for H$_2$O$_2$ in the martian atmosphere becomes:
\[
\frac{dN_a(t)}{dt} = P - lN_a(t) - \frac{1}{4}cN_a(t) + \frac{1}{4}cfn_c(0)
\]
Since it is the long term equilibrium distribution of H$_2$O$_2$ that is of interest, this equation is solved for the steady state,
\[
\lim_{t \to \infty} \frac{dN_a(t)}{dt} = 0 \text{ and } \lim_{t \to \infty} N_a(t) = N_a
\]
and the atmosphere equation becomes
\[
P - lN_a - \frac{1}{4}cN_a + \frac{1}{4}cfn_c(0) = 0
\]
For the purposes of coupling this equation to the equation describing H$_2$O$_2$ transport through the soil, concentrations are expressed in terms of number densities. Thus,
\[
P - lHn_a(0) - \frac{1}{4}cn_a(0) + \frac{1}{4}cfn_c(0) = 0 \quad (3.13)
\]
solving for $n_a(0)$,

$$(lH + \frac{1}{4}c)n_a(0) = P + \frac{1}{4}cfn_c(0)$$

$$n_a(0) = \frac{P + \frac{1}{4}cfn_c(0)}{lH + \frac{1}{4}c} \quad (3.14)$$

Here, the atmospheric concentration at the surface is expressed in terms of the atmospheric production and loss rates, as well as by the fluxes into and out of the soil. The atmospheric concentration is a function of the vapor phase concentration in the soil pore spaces, and thus also a function of the adsorbed phase concentration, through the relation $n_c(z) = \frac{1}{\epsilon}n_v(z)$.

In order to calculate the adsorbed H$_2$O$_2$ concentration as a function of depth, it is necessary to model the diffusion and destruction of H$_2$O$_2$ through the soil, with boundary conditions consistent with the atmosphere model. It is known that H$_2$O$_2$ is catalytically destroyed in the presence of Fe and water (Schumb 1955), the environment in which it exists in the martian soil. Catalytic destruction may occur once the H$_2$O$_2$ has been adsorbed onto the iron rich soil grains. In this model, the destruction rate is expressed in terms of a lifetime, $\tau$, so that the destruction rate of H$_2$O$_2$ in the soil is given by

$$\frac{n_c(z,t)}{\tau}$$

The diffusion equation for H$_2$O$_2$ through the soil is

$$\epsilon \frac{\partial n_v(z,t)}{\partial t} + \frac{\partial n_c(z,t)}{\partial t} = -\frac{\partial F(z,t)}{\partial z} - \frac{n_c(z,t)}{\tau} \quad (3.15)$$

where:

$\epsilon$ is the porosity of the soil.

Transport into the soil proceeds by diffusion, given by Fick's Law,

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

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where:

\( D \) is the diffusion coefficient.

Using the phase partitioning factor, \( f \), the diffusion equation is rewritten as

\[
\frac{\partial n_c(z,t)}{\partial t} = Df \frac{\partial^2 n_c(z,t)}{\partial z^2} - \frac{n_c(z,t)}{\tau}
\]

which is subject to the boundary conditions,

BC 1

\[
\lim_{z \to \infty} n_c(z,t) = 0
\]

BC 2

\[
-D \left. \frac{\partial n_v(z,t)}{\partial z} \right|_{z=0} = F_i - F_o
\]

or,

\[
-D \left. \frac{\partial n_c(z,t)}{\partial z} \right|_{z=0} = \frac{1}{4} c n_a(0) - \frac{1}{4} c f n_c(0)
\]

The first boundary condition assures that the integrated concentration remains finite. The second boundary condition is at the soil/atmosphere interface, where the net flux into the soil from the atmosphere must be equal to the diffusion/destruction flux. From the atmosphere equation, it was shown that the atmospheric concentration was a function of the concentration at the soil surface. Similarly, the soil concentration is coupled to the atmospheric concentration through BC 2. Again, a steady state solution to the soil diffusion equation is sought,

\[
\lim_{t \to \infty} \frac{\partial n_c(z,t)}{\partial t} = 0 \quad \text{and} \quad \lim_{t \to \infty} n_c(z,t) = n_c(z)
\]

The steady state soil equation is then

\[
\frac{\partial^2 n_c(z)}{\partial z^2} - \frac{1}{D\tau f} n_c(z) = 0 \quad (3.16)
\]
Solutions have the form

\[ n_c(z) = Ae^{-z/\sqrt{D\tau f}} + Be^{z/\sqrt{D\tau f}} \]

Applying BC 1,

\[ \lim_{z \to \infty} n_c(z) = 0 \]

so that \( B = 0 \). The solution is therefore

\[ n_c(z) = n_c(0)e^{-z/\sqrt{D\tau f}} \quad (3.17) \]

Applying BC 2,

\[ -Df \frac{\partial n_c(z,t)}{\partial z} \bigg|_{z=0} = \frac{1}{4} cn_a(0) - \frac{1}{4} cf n_c(0) \]

This is solved for \( n_c(0) \).

\[ n_c(0) = \frac{\frac{1}{4} \left( \frac{\tau f}{D} \right)^{\frac{1}{2}} \frac{1}{4} cn_a(0)}{\left( \frac{\tau f}{D} \right)^{\frac{1}{2}} \frac{1}{4} c + 1} \quad (3.18) \]

There are now two coupled algebraic Equations, 3.14 and 3.18, that may be solved simultaneously to yield both the soil adsorbed phase concentration at the surface, and the atmospheric concentration, in terms of production, loss and transport coefficients. Equation 3.14 is substituted into Equation 3.18 to obtain an expression for \( n_c(0) \):

\[ n_c(0) = \frac{P}{lHf + f \left( \frac{D}{\tau f} \right)^{\frac{1}{2}} \left[ \frac{4H}{c} + 1 \right]} \quad (3.19) \]

From this, the concentration of \( \text{H}_2\text{O}_2 \) in the soil at any depth may be calculated from the solution to the soil diffusion Equation 3.17. The \( \frac{1}{c} \) folding depth may be found in the exponent, and is

\[ \delta = \sqrt{D\tau f} \quad (3.20) \]

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For the density case, the average concentration in the top 4 cm is specified. If this concentration is denoted as \( n_i \), and the depth to which the concentration is averaged is \( z_i \),

\[
n_i = \frac{1}{z_i} \int_0^{z_i} n(z)dz
\]
or

\[
n_i = n_c(0) \frac{\delta}{z_i} \left[ 1 - e^{-\frac{z_i}{\delta}} \right]
\]  
(3.21)

For \( z_i \gg \delta \),

\[
n_c(0) = \frac{n_iz_i}{(D\tau f)^{\frac{1}{2}}}
\]

Substituting this into Equation 3.19, the result is a quadratic equation in \( n_c(0) \), which yields

\[
n_c(0) = \frac{\sqrt{(n_iz_iHf)^2 + 4PDfn_iz_i\left[ \frac{4H}{c} + 1 \right]} - n_iz_iHf}{2Df\left[ \frac{4H}{c} + 1 \right]}
\]  
(3.22)

Equation 3.19 may also be rearranged to obtain an expression for the lifetime of \( \text{H}_2\text{O}_2 \) in the soil,

\[
\tau = \frac{D}{f} \left( \frac{f\left[ \frac{4H}{c} + 1 \right]}{\frac{P}{n_c(0)} - lHf} \right)^2
\]  
(3.23)

The concentration of \( \text{H}_2\text{O}_2 \) in the atmosphere at the surface may be calculated from Equation 3.14,

\[
n_a(0) = \frac{P + \frac{1}{4}cfn_c(0)}{lH + \frac{1}{4}c}
\]

For the lifetime case, \( n_c(0) \) and \( \delta \) are calculated directly from Equations 3.19 and 3.20, and the average concentration of \( \text{H}_2\text{O}_2 \) in the top layer of soil is calculated from equation 3.21.
3.4.2 Numerical Results

Density Case

For the density case, $\tau$ is treated as a free parameter, and the average surface soil concentration is constrained to be 30 nmoles cm$^{-3}$. To calculate the lifetime, $\tau$, the characteristic depth, $\delta$, and the atmospheric number density, $n_a(0)$, the following values are used:

\[
D = 0.0163 \text{ cm}^2 \text{ sec}^{-1} \\
f = 8 \times 10^{-10} \\
P = 4.183 \times 10^9 \text{ cm}^{-2} \text{ sec}^{-1} \\
l = 2.5 \times 10^{-5} \text{ sec}^{-1} \\
H = 1.8 \times 10^6 \text{ cm} \\
c = 3.658 \times 10^4 \text{ cm sec}^{-1}
\]

For this case, the following results are obtained:

The lifetime of $\text{H}_2\text{O}_2$ in the soil is found to be:

\[
\tau = 3.01 \times 10^8 \text{ sec} \simeq 10 \text{ years}
\]

and the characteristic depth is:

\[
\delta = 0.063 \text{ cm}
\]

The atmospheric concentration at the surface is:

\[
n_a(0) = 9.242 \times 10^8 \text{ cm}^{-3}
\]
which is slightly more than the concentration of vapor phase H₂O₂ in the pores of the soil. Since \( n_v(0) = f n_c(0) \),

\[
n_v(0) = 9.241 \times 10^8 \text{ cm}^{-3}
\]

This difference between vapor phase concentrations in the atmosphere and soil is driven by the diffusion and destruction flux, parameterized by \( D \) and \( \tau_f \). It is illuminating to calculate the fluxes involved in the problem. They are:

- Atmospheric production flux \( 4.183 \times 10^{10} \text{ cm}^2 \text{ sec}^{-1} \)
- Atmospheric loss flux \( 4.159 \times 10^{10} \text{ cm}^2 \text{ sec}^{-1} \)
- Flux into the soil \( 8.452 \times 10^{12} \text{ cm}^2 \text{ sec}^{-1} \)
- Flux out of the soil \( 8.452 \times 10^{12} \text{ cm}^2 \text{ sec}^{-1} \)
- Diffusion/destruction flux \( 2.402 \times 10^8 \text{ cm}^2 \text{ sec}^{-1} \)

where the diffusion/destruction flux is given by

\[
F_d = \left( \frac{D}{\tau_f} \right)^{1/2} n_v(0) = \left( \frac{D}{\tau_f} \right)^{1/2} f n_c(0)
\]  

(3.24)

The soil acts as a sink, driven by a gradient that is a function of a deposition term and a diffusion/destruction term. It can be seen that although the net flux into the soil is on the order of the atmospheric column production rate, the net effect on atmospheric concentration is small. That is, the atmosphere is weakly coupled to the soil, but provides enough H₂O₂ to the surface to account for the Viking LR experiment results. Figure 3.7 shows the exponential depth profile of H₂O₂ for the density case.
Lifetime Case

For the lifetime case, the concentration of $\text{H}_2\text{O}_2$ at the surface is treated as a free parameter, and the lifetime against catalytic destruction is $3.15 \times 10^{12}$ seconds. To calculate the characteristic depth, $\tau$, the average concentration in the top layer, $n_l$, and the atmospheric number density at the surface, the following values are used:

$$D = 0.0163 \text{ cm}^2 \text{ sec}^{-1}$$
$$\tau = 3.15 \times 10^{12} \text{ sec}$$
$$f = 8 \times 10^{-10}$$
$$P = 4.183 \times 10^9 \text{ cm}^{-2} \text{ sec}^{-1}$$
$$l = 2.5 \times 10^{-5} \text{ sec}^{-1}$$
$$H = 1.8 \times 10^6 \text{ cm}$$
$$c = 3.658 \times 10^4 \text{ cm sec}^{-1}$$

For this case, the following results are obtained:

The $\frac{1}{e}$ characteristic depth is:

$$\delta = 6.401 \text{ cm}$$

The average concentration of adsorbed $\text{H}_2\text{O}_2$ in the top 4 cm of soil is

$$n_l = 1434.62 \text{ nmoles cm}^{-3}$$

The atmospheric number density at the surface is,

$$n_a(0) = 9.294 \times 10^8 \text{ cm}^{-3}$$
which is very close to the concentration of vapor phase \( \text{H}_2\text{O}_2 \) in the pore space of the soil. Since \( n_v(0) = fn_e(0) \),

\[
n_v(0) = 9.294 \times 10^8 \text{ cm}^{-3}
\]

Calculating the fluxes involved for the lifetime case,

Atmospheric production flux \( 4.1827 \times 10^{10} \text{ cm}^2 \text{ sec}^{-1} \)

Atmospheric loss flux \( 4.1825 \times 10^{10} \text{ cm}^2 \text{ sec}^{-1} \)

Flux into the soil \( 8.500 \times 10^{12} \text{ cm}^2 \text{ sec}^{-1} \)

Flux out of the soil \( 8.500 \times 10^{11} \text{ cm}^2 \text{ sec}^{-1} \)

Diffusion/destruction flux \( 2.36 \times 10^6 \text{ cm}^2 \text{ sec}^{-1} \)

where the diffusion/destruction flux is again given by

\[
F_d = \left( \frac{D}{\tau_f} \right)^{1/2} n_v(0) = \left( \frac{D}{\tau_f} \right)^{1/2} fn_e(0)
\]  

(3.25)

Once again, the soil acts as a sink, driven by a gradient that is a function of a deposition term and a diffusion/destruction term. Due to a longer lifetime, the diffusion/destruction processes are weak compared to the atmospheric production and loss. The diffusion flux is 4 orders of magnitude lower than the atmospheric production flux. For the lifetime case, coupling between the soil and atmosphere is very weak, and the atmospheric concentration may be given simply by

\[
n_a(0) = \frac{P}{lH}
\]

This may be considered the maximum possible concentration for atmospheric \( \text{H}_2\text{O}_2 \), since the soil is virtually passive. Since the gradient at the soil surface is not strong, the vapor phase concentration of \( \text{H}_2\text{O}_2 \) in the pore spaces is nearly

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the same as the atmospheric concentration. Through the phase partitioning relation, \( f = \frac{n_c(0)}{n_c(0)} \), the concentration of adsorbed \( \text{H}_2\text{O}_2 \) is simply

\[
n_c(0) = \frac{P}{lHf}
\]

or about 1929.34 nmoles cm\(^{-3} \). By considering lifetimes as long as \( 10^5 \) years, it can be seen that the soil concentration is maximized to a value about two orders of magnitude higher than that inferred from the LR experiment. The exponential depth profile of \( \text{H}_2\text{O}_2 \) for the lifetime case is shown in Figure 3.8.

In order to investigate the behaviour of the model for a wide range of \( \text{H}_2\text{O}_2 \) lifetimes, the average surface concentration, characteristic depth, and atmospheric number density are plotted as a function of lifetime in Figures 3.9, 3.10 and 3.11.

### 3.4.3 Discussion

When the concentration of \( \text{H}_2\text{O}_2 \) adsorbed at the surface is assumed to be 30 nmoles cm\(^{-3} \), the model predicts a \( \text{H}_2\text{O}_2 \) lifetime of about 10 years and a characteristic depth of less than a centimeter. With this high a destruction rate, net flux into the soil is close to the atmospheric production rate, and atmospheric concentrations are very slightly reduced. Alternately, when lifetimes are assumed to be very long, on the order of \( 10^5 \) years, the model predicts a concentration of \( \text{H}_2\text{O}_2 \) adsorbed at the surface of about 2000 nmoles cm\(^{-3} \). The characteristic depth calculated with such a lifetime is 6.4 cm. For extremely long lifetimes, the depth to layers with extremely low \( \text{H}_2\text{O}_2 \) concentrations is only on the order of centimeters. The surface concentrations are not significantly higher,
however, than those for the case with a short lifetime, due to equilibrium with the atmosphere. For a wide range of lifetimes, the model results are consistent with using $\text{H}_2\text{O}_2$ as an explanation of the Viking LR experiment results. Furthermore, if $10^5$ years is considered as an upper bound for $\text{H}_2\text{O}_2$ lifetime, then 6.4 cm may be considered an upper bound for the value of the $\frac{1}{e}$ folding depth. This would indicate that if $\text{H}_2\text{O}_2$ is the primary oxidant in the martian soil, destruction of organic material may cease at depths approaching a meter.
Figure 3.8  Lifetime Case — Linear Coupled Model
3.5 Nonlinear Coupled Soil/Atmosphere Model

3.5.1 Introduction

The models presented in the previous sections, of the transport of H$_2$O$_2$ through the martian soil and atmosphere have incorporated either an ad hoc soil/atmosphere coupling or have ignored the division of H$_2$O$_2$ into adsorbed and vapor phases. Presented here is an analytical model that predicts atmospheric and soil concentrations of H$_2$O$_2$ based on a net flux of H$_2$O$_2$ into the soil and on adapting empirically derived adsorption isotherms for water 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 a standard lapse rate. Concentrations in the soil are determined from a diffusion equation that incorporates catalytic destruction of adsorbed H$_2$O$_2$. Since diffusion is accomplished by the vapor phase, the adsorption isotherms are used to establish phase partitioning between the absorbed (fixed) and vapor (mobile) phases. The soil diffusion equation is coupled to the atmosphere equation through a flux boundary condition at the soil/atmosphere interface. The net flux of H$_2$O$_2$ 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$_2$O$_2$ phases must be known. The least well determined of these is the loss rate of adsorbed H$_2$O$_2$ due to heterogenous catalysis. The lifetime of H$_2$O$_2$ adsorbed in the soil is therefore taken as a free parameter, and the general solution with respect to this parameter may be calculated.

**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 $6.5 \times 10^7$ cm$^{-3}$ for the number density of HO$_2$ (Kong and McElroy 1977), and a scale height, H, of 18 km, the column production rate of H$_2$O$_2$ is

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

**Atmospheric Loss**

The loss of H$_2$O$_2$ 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

\[ l = 2.5 \times 10^{-5} \text{ sec}^{-1} \]

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.

\[ n_4(0) = \frac{P}{lH} = 9.3 \times 10^8 \text{ cm}^{-3} \]

which is in rough agreement with the number density calculated by Kong and McElroy (1977), \(2 \times 10^9\) cm\(^{-3}\).

**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 downwards, by the adsorption of H\(_2\)O\(_2\) 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\(_2\)O\(_2\) 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 total volume to pore space 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 (Scatterfield 1970, Smoluchowski 1967). The molecular diffusion coefficient is given analytically as $D_m = \frac{\epsilon}{\tau} D_o$ where $D_o$ is the gas-gas diffusion coefficient, $\epsilon$ is the soil porosity, and $\tau$ is the soil porosity (Flood 1967). The value of the molecular diffusion coefficient for $\text{H}_2\text{O}_2$ in $\text{CO}_2$ at an average surface temperature of 215 K is $D_m = 0.678 \text{ cm}^2 \text{ sec}^{-1}$.

If pores are mostly smaller than the mean free path, molecular collisions with the pore walls dominate the transport of $\text{H}_2\text{O}_2$ a process known as Knudsen diffusion. The average pore size may be taken to be 1 $\mu$m (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 $\mu$m. Therefore, Knudsen diffusion is the dominant transport mechanism for $\text{H}_2\text{O}_2$ through the martian soil at this temperature. The Knudsen diffusion coefficient is given analytically as $D_K = \frac{4 \epsilon r_o}{9 \tau} \left[ \frac{2kT}{\pi m} \right]$ where $r_o$ is the average pore radius and $m$ is the $\text{H}_2\text{O}_2$ molecular mass (Fanale et al., 1986). The value of the Knudsen diffusion coefficient for $\text{H}_2\text{O}_2$ in the martian soil is calculated to be $D_K = 0.0163 \text{ cm}^2 \text{ sec}^{-1}$. 

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Soil Loss

The thermal sensitivity of the Viking LR experiment was used to estimate a lifetime of $10^5$ years for the LR oxidant in the martian soil (Levin and Straat 1979, Chyba et al. 1989). Laboratory work on the catalytic destruction rate of H$_2$O$_2$ in a ferrous environment, however, indicates much shorter lifetimes, on the order of minutes (Schumb 1955). Because of the uncertainty of the actual chemistry of the martian surface, catalytic destruction rates for H$_2$O$_2$ 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 lifetimes.

Phase Partitioning

Empirically derived isotherms for the adsorption of H$_2$O in the martian soil yield a power law relationship between adsorbed and vapor phases. The vapor pressure curves for H$_2$O and H$_2$O$_2$ are fairly similar at low temperatures, as are the molecular dipole moments. However, the concentrations of H$_2$O in the martian soil are much higher than those of H$_2$O$_2$ and it should be expected that there is some variation in the adsorption isotherms between H$_2$O and H$_2$O$_2$. Since specific laboratory data on the adsorption of H$_2$O$_2$ under martian conditions is lacking, the isotherms for H$_2$O are used to describe the phase partitioning for H$_2$O$_2$. The empirical relationship between adsorbed and vapor phases is given as

$$n_c = S(T)n_v^{\frac{1}{2}}$$
where \( n_c \) is the adsorbed phase concentration and \( n_v \) is the vapor phase concentration. At 215 K, \( S \) is constant and is calculated to be

\[
S(215) = 4.757 \times 10^{12} \text{ cm}^{-2}
\]

For a soil that is a poor atmospheric sink, the amount of adsorbed \( \text{H}_2\text{O}_2 \) may be estimated, assuming that \( \text{H}_2\text{O}_2 \) in the soil pore spaces is in pressure equilibrium with the atmosphere.

\[
n_c = S(T)n_v^{1/2} = 240 \text{ nanomoles cm}^{-3}
\]

This represents a maximum amount of \( \text{H}_2\text{O}_2 \) at the surface, assuming soil losses are negligible.

For the purpose of comparing the Viking LR experiment results with the model, the surface concentration of 30 nmoles cm\(^{-3}\) 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 \( \text{H}_2\text{O}_2 \) consistent with atmospheric/soil equilibrium, as shown above, is a factor of eight higher. Therefore, soil diffusion and loss rates that do not deplete the surface by more than a factor of eight 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, it is valuable to know what value of lifetime is necessary to achieve such a steady state surface concentration. It is also important to know how much of a sink the soil is for atmospheric
H$_2$O$_2$ under such constraints. The model is solved in the Lifetime case for a lifetime of $10^5$ years. By considering the adsorbed H$_2$O$_2$ to be relatively stable on Mars, calculations are made for the average surface concentration in the top 4 cm. Again, the degree to which the soil is a sink for H$_2$O$_2$ is calculated. The third case examined is the Loss Regime Case. If H$_2$O$_2$ 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$_2$O$_2$. The lifetime required for the martian soil and atmosphere to be sinks of equal magnitude is calculated.

3.5.2 The Model

The model is comprised 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$_2$O$_2$ enters in the soil equation.

The Atmosphere Equation

If $N_a$ is the column density of H$_2$O$_2$ in the martian atmosphere,

$$\frac{dN_a}{dt} = P - lN_a(t) - F_i + F_o$$  \hspace{1cm} (3.26)

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

$$n_a(z) = n_a(0)e^{-\frac{z}{H}}$$
where \( n_a(z) \) is the number density of \( \text{H}_2\text{O}_2 \) as a function of altitude and \( H \) is the density scale height. The atmosphere equation becomes

\[
H \left. \frac{\partial n_a(z, t)}{\partial t} \right|_{z=0} = P - lHn_a(0) - F_i + F_o
\]

Since it is the long term equilibrium distribution of \( \text{H}_2\text{O}_2 \) that is of interest, this equation is solved for the steady state

\[
\lim_{t \to \infty} \frac{\partial n_a(z, t)}{\partial t} = 0 \quad \text{and} \quad \lim_{t \to \infty} n_a(0, t) = n_a(0)
\]

and the steady state atmosphere equation is

\[
P - lHn_a(0) - F_i + F_o = 0
\]

The flux into the soil is assumed to be the rate at which molecules impinge upon the surface due to 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 \( \text{H}_2\text{O}_2 \) in the pore spaces near the surface.

\[
F_o = \frac{1}{4}cn_v(0)
\]

With these substitutions, the atmosphere equation becomes

\[
P - lHn_a(0) = \frac{1}{4}cn_a(0) - \frac{1}{4}cn_v(0)
\]  (3.27)

Solving for the atmospheric concentration at the surface,

\[
n_a(0) = \frac{P + \frac{1}{4}cn_a(0)}{lH + \frac{1}{4}c}
\]  (3.28)
The Soil Diffusion Equation

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

$$\epsilon \frac{\partial n_v(z,t)}{\partial t} + \frac{\partial n_c(z,t)}{\partial t} = -\frac{\partial F(z,t)}{\partial z} - \frac{n_c(z,t)}{\tau}$$  \hspace{1cm} (3.29)$$

where $\epsilon$ is the porosity of the soil, and $F$ is the flux. Transport in the soil proceeds 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 diffusion equation is rewritten,

$$\epsilon \frac{\partial n_v}{\partial t} + \frac{\partial n_c}{\partial t} = D \frac{\partial^2 n_v}{\partial t^2} - \frac{S}{\tau n_c}$$

Again, the steady state solution is sought,

$$\lim_{t \to \infty} \frac{\partial n_c}{\partial t} = \lim_{t \to \infty} \frac{\partial n_v}{\partial t} = 0 \quad \text{and} \quad \lim_{t \to \infty} n_v(z,t) = n_v(z)$$

The steady state isothermal soil diffusion equation becomes

$$\frac{d^2 n_v}{dz^2} = \frac{S}{D\tau} n_v^{\frac{1}{2}}$$ \hspace{1cm} (3.30)$$

with boundary conditions

**BC 1**

$$\lim_{z \to \text{large}} n_v(z) = 0$$

**BC 2**

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

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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 equation may be integrated once to give

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

**Boundary Condition 1** At some depth, \( n_v \rightarrow 0 \). However, the gradient is also expected to go to zero. Therefore, applying the first boundary implies that \( C_1 = 0 \). Then the first integral becomes:

\[ \frac{dn_v}{dz} = \pm \frac{2}{\sqrt{3}} \left( \frac{S}{D\tau} \right)^{\frac{1}{2}} n_v^{\frac{3}{2}} \quad (3.31) \]

It is expected that the concentration will decrease with depth. Therefore the gradient is negative. Integrating again,

\[ n_v(z) = \left[ C_2 - \frac{1}{2\sqrt{3}} \left( \frac{S}{D\tau} \right)^{\frac{1}{2}} z \right]^4 \]

where \( C_2 \) may be identified as \( n_v^{\frac{3}{4}}(0) \) and must be determined from the second boundary condition. Since the quantity of interest is the concentration of adsorbed \( \text{H}_2\text{O}_2 \), the phase partitioning function derived in Section 3.2.1 is used.

\[ n_c = Sn_v^{\frac{1}{2}} \]

The general solution to the soil diffusion equation, in terms of the adsorbed phase concentration is thus

\[ n_c(z) = \left[ n_c^{\frac{1}{2}}(0) - \left( \frac{S^2}{12D\tau} \right)^{\frac{1}{2}} z \right]^2 \quad (3.32) \]
Boundary Condition 2  From Equation 3.31,

\[
\frac{dn_v}{dz} \bigg|_{z=0} = - \left( \frac{4S}{3D\tau} \right)^{\frac{1}{3}} n_v^3(0)
\]

Then the net flux of H$_2$O$_2$ into the soil is, by the second boundary condition,

\[-D \frac{dn_v}{dz} \bigg|_{z=0} = \left( \frac{4S}{3D\tau} \right)^{\frac{1}{3}} n_v^3(0) = F_i - F_o
\]

in terms of atmospheric production and loss terms,

\[\left( \frac{4S}{3D\tau} \right)^{\frac{1}{3}} n_v^3(0) = P - lHn_a(0)\]

Equation 3.28 for $n_a(0)$, derived from the steady state atmosphere equation is substituted into the above equation

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

Expressed as a polynomial in $n_v(0)$, this is

\[n_v(0) + \left( \frac{64DS}{3c^2\tau} \right)^{\frac{1}{3}} \left[ 1 + \frac{c}{4lH} \right] n_v^3(0) - \frac{P}{lH} = 0\]

Again, since it is the concentration of adsorbed H$_2$O$_2$ that is of interest, the phase partitioning function, Equation 3.1, is used to convert the polynomial in $n_v(0)$ to one in $n_c(0)$,

\[n_c^2(0) + n_c^2 \left( \frac{64DS^2}{3c^2\tau} \right)^{\frac{1}{3}} \left[ 1 + \frac{c}{4lH} \right] - \frac{PS^2}{lH} = 0 \quad (3.33)\]

which is solved numerically.

Applying the second boundary condition has allowed the calculation of the adsorbed phase concentration for given lifetimes. The depth profile of H$_2$O$_2$ in the soil is given by the general solution, Equation 3.32. Other physically significant quantities may also be calculated from $n_c(0)$.  

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**Extinction Depth**  The general solution to the soil diffusion equation, equation 3.32, shows that the concentration of adsorbed \( \text{H}_2\text{O}_2 \) goes to zero at a finite depth. Due to the nonlinear phase partitioning, \( n_c = S(T)n_c^\frac{1}{2} \), as the concentration of mobile \( \text{H}_2\text{O}_2 \) decreases with depth, the concentration of adsorbed \( \text{H}_2\text{O}_2 \) decreases at the square of this rate. The result is a rapid decrease in adsorbed \( \text{H}_2\text{O}_2 \) with depth. The solution,

\[
n_c(z) = \left[ n_c^\frac{1}{2}(0) - \left( \frac{S^2}{12D_T} \right)^{\frac{1}{2}} z \right]^2
\]

goess to zero at a finite depth, \( z_e \). For \( n_c(z_e) = 0 \),

\[
n_c^\frac{1}{2}(0) - \left( \frac{S^2}{12D_T} \right) z_e = 0
\]

So that the extinction depth is

\[
z_e = \left( \frac{12D_T}{S^2} \right)^{\frac{1}{2}} n_c^\frac{1}{2}(0)
\]  (3.34)

**Average Surface Concentration**  The physically observable concentration of \( \text{H}_2\text{O}_2 \) 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

\[
n_l = \frac{1}{z_l} \int_0^{z_l} n_c(z) \, dz \quad z_l < z_e
\]

Since the concentration of adsorbed \( \text{H}_2\text{O}_2 \) 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,

\[
n_l = \begin{cases} 
\frac{2}{z_l} \left[ n_e^\frac{1}{3} (0) - \left( \frac{s^2}{12D_r} \right)^{\frac{1}{3}} z \right]^3 \left( -\frac{s^2}{12D_r} \right)^{\frac{1}{3}} \bigg|_0^{z_l} & z_l < z_e \\
\frac{2}{z_l} \left[ n_e^\frac{1}{3} (0) - \left( \frac{s^2}{12D_r} \right)^{\frac{1}{3}} z \right]^3 \left( -\frac{s^2}{12D_r} \right)^{\frac{1}{3}} \bigg|_0^{z_e} & z_l \geq z_e 
\end{cases}
\]

The average concentration of adsorbed \( \text{H}_2\text{O}_2 \) in the top 4 cm of soil is

\[
n_l = \begin{cases} 
\left( \frac{4D_r}{3S^2} \right)^{\frac{1}{3}} \frac{n_e^\frac{2}{3} (0)}{z_l} & z_l < z_e \\
\left( \frac{4D_r}{3S^2} \right)^{\frac{1}{3}} \frac{n_e^\frac{2}{3} (0)}{z_l} \left[ \left( \frac{z_l}{z_e} - 1 \right)^3 + 1 \right] & z_l \geq z_e 
\end{cases}
\]

(3.35)

**Atmospheric Number Density**  Equation 3.28 for the atmospheric number density at the surface may be expressed in terms of the \( \text{H}_2\text{O}_2 \) adsorbed phase concentration in the soil via the phase partitioning function

\[
n_a(0) = \frac{P + \frac{1}{4} S n_e^2 (0)}{lH + \frac{1}{4} c} 
\]

(3.36)

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

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

\[
F_{\text{soil}} = F_i - F_o = \left( \frac{4DS}{3\tau} \right)^{\frac{1}{3}} n_e^{\frac{2}{3}} (0) 
\]

Once again, this quantity may be expressed in terms of the adsorbed phase concentration of \( \text{H}_2\text{O}_2 \) through the phase partitioning function

\[
F_{\text{soil}} = \left( \frac{4D}{3\tau S^2} \right)^{\frac{1}{3}} n_e^{\frac{2}{3}} (0) 
\]

(3.37)
This completes the general solution to the model, which has allowed the computation of 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 \( \text{H}_2\text{O}_2 \) into the soil, in terms of the soil lifetime parameter.

### 3.5.3 Results

**Density Case**

If it is assumed that \( \text{H}_2\text{O}_2 \) was responsible for the evolution of \( \text{CO}_2 \) in the Viking Labeled Release experiment, the average concentration of \( \text{H}_2\text{O}_2 \) in the top 4 cm may be taken to be about 30 nmoles cm\(^{-3}\). This concentration is achieved in the model with a \( \text{H}_2\text{O}_2 \) lifetime in the soil of

\[
\tau = 1.79 \times 10^9 \text{ sec} \approx 57 \text{ terrestrial years}
\]

The extinction depth is calculated from Equation 3.34 to be

\[
z_e = 1.50 \text{ cm}
\]

and the atmospheric number density at the surface is calculated from equation 3.36 to be

\[
n_a(0) = 9.286 \times 10^8 \text{ cm}^{-3}
\]

This may be compared with the number density that is obtained with the assumption that the soil is passive with respect to \( \text{H}_2\text{O}_2 \)

\[
n_a = 9.295 \times 10^8 \text{ cm}^{-3}
\]

It can be seen that with an average surface concentration of 30 nmoles cm\(^{-3}\), the lifetime of 57 years yields a very shallow depth and a very passive soil.
Lifetime Case

Assuming $\text{H}_2\text{O}_2$ to be responsible for the Viking Labeled Release experiment results, Chyba et al. (1989) calculated a 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 $\text{H}_2\text{O}_2$ in the top 4 cm is found to be

$$z_l = 225.45 \text{ nmoles cm}^{-3}$$

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,

$$z_e = 62.85 \text{ cm}$$

and the atmospheric number density reflects the fact that the soil is even more passive,

$$n_a(0) = 9.295 \times 10^8 \text{ nmoles cm}^{-3}$$

which is identical to that obtained for a completely passive surface, to within 4 significant figures.

Loss Regime Case

The model results for the Density and Lifetime Cases show that for a wide range of lifetimes of $\text{H}_2\text{O}_2$ in the soil, the atmospheric number density is effected only
slightly. However, it is interesting to explore the behaviour of the model for regimes where the soil may play a more active role in the destruction of H$_2$O$_2$. 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$_2$O$_2$ sinks of equal magnitude. This condition is met when the lifetime of H$_2$O$_2$ in the soil is

\[ \tau = 40 \text{ minutes} \]

The resulting average surface concentration is very small,

\[ n_s = 0.002 \text{ nmoles cm}^{-3} \]

and the extinction depth is very shallow

\[ z_e = 1.5 \times 10^{-3} \text{ cm} \]

Thus it is seen that for the soil to represent a sink for H$_2$O$_2$ that is comparable with the atmosphere, surface concentrations will be extremely small, with all the H$_2$O$_2$ residing very close to the surface.

### 3.5.4 Discussion

The nonlinear relationship between adsorbed and vapor phase H$_2$O$_2$ results in a parabolic depth profile for the solution to the soil diffusion equation. This curious result implies that H$_2$O$_2$ 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 Figures 3.12 and 3.13,
respectively. 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 $\text{H}_2\text{O}_2$ against heterogenous catalytic destruction under martian conditions is not well constrained, the model is characterized in terms of this parameter. Quantities of physical interest are the average concentration of $\text{H}_2\text{O}_2$ 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 Figures 3.14, 3.15 and 3.16.
Figure 3.12
Density Case — Nonlinear Coupled Model

$H_2O_2$ Depth Profile

Concentration (nmoles cm$^{-2}$)

Depth (cm)
Figure 3.13  Lifetime Case -- Nonlinear Coupled Model
Figure 3.14  H$_2$O$_2$ Concentration vs. Lifetime — Nonlinear Coupled Model
Figure 3.15  Depth vs. Lifetime — Nonlinear Coupled Model
Figure 3.16 Atmospheric Concentration vs. Lifetime — Nonlinear Coupled Model
3.6 Conclusions

The depth predictions of the two coupled soil/atmosphere models are similar to each other in magnitude. Due to different analytical forms for the soil diffusion equations, however, the nature of the solutions is different. With the simple assumption of linear phase partitioning, an exponential decay of $H_2O_2$ with depth results. In the more realistic treatment of phase partitioning, a complete extinction of $H_2O_2$ occurs at a finite depth. Net fluxes of $H_2O_2$ into the soil are 5 orders of magnitude less than the ad hoc assumptions incorporated into the uncoupled models. The result is that when soil/atmosphere coupling is considered, less $H_2O_2$ is supplied to the soil.

With a model of $H_2O_2$ distribution in the martian soil and atmosphere, the following three questions may be addressed:

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 will it be possible 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, the average concentration of $H_2O_2$ in the top 4 cm of the soil must be constrained 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 57 terrestrial
years. In this sense, the model is not inconsistent with the additional inference of a H$_2$O$_2$ lifetime of $10^5$ years. Additionally, at these soil concentrations and lifetimes, it is seen that the soil is a poor sink for H$_2$O$_2$. Therefore, atmospheric concentrations of H$_2$O$_2$ predicted by this model are consistent with more complex atmospheric models that assume a passive surface. It may be concluded that as long as the lifetime of H$_2$O$_2$ in the soil is greater than 57 terrestrial years, the model is consistent with Viking Biology experiment results. For any value of lifetime of H$_2$O$_2$ in the soil that is consistent with the Viking Biology experiment results, the soil is a poor sink for H$_2$O$_2$ compared with the atmosphere. Unless the lifetime is on the order of an hour or less, the atmosphere may be considered the primary sink for H$_2$O$_2$. Given this condition, more complex models of H$_2$O$_2$ 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$_2$O$_2$ was less than 63 cm. 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$_2$O$_2$ may penetrate. If H$_2$O$_2$ is the primary agent responsible for the oxidation of organics in the martian soil, it may be inferred that organic compounds may still exist just below approximately 1 meter.
Chapter 4

References

Anderson, D.M., and A.R. Tice, The Analysis of Water in the Martian Regolith,  

Ball, B. C., Modeling of Soil Pores as Tubes Using Gas Permeabilities, Gas  

Ballou, E.V., P.C. Wood, T. Wydeven, M.E. Lehwalt, R.E. Mack, Chemical  
Interpretation of Viking Lander 1 Life Detection Experiment, *Nature* 271,  

Banin, A. and L. Margulies, Simulation of Viking biology Experiments Suggests  
Smectites not Palagonite, as Martian Soil Analogs, *Nature* 305, 523-526,  
1983.

Banin, A. and J. Rishpon, Smectite Clays in Mars Soil: Evidence for their  


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Ponnampalam, C., A. Shimoyama, M. Yamada, T. Hobo, and R. Pal, Possible


