1991

The destruction of organic compounds on Mars

Mark A. Bullock
San Jose State University

Follow this and additional works at: https://scholarworks.sjsu.edu/etd_theses

Recommended Citation

Bullock, Mark A., "The destruction of organic compounds on Mars" (1991). *Master's Theses*. 183.
DOI: <https://doi.org/10.31979/etd.zq36-g9bf>
https://scholarworks.sjsu.edu/etd_theses/183

This Thesis is brought to you for free and open access by the Master's Theses and Graduate Research at SJSU ScholarWorks. It has been accepted for inclusion in Master's Theses by an authorized administrator of SJSU ScholarWorks. For more information, please contact scholarworks@sjsu.edu.

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

U·M·I

University Microfilms International
A Beil & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600

Order Number 1345790

The destruction of organic compounds on Mars

Bullock, Mark Alan, M.S.

San Jose State University, 1991

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

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

Mark A. Bullock
August 1991

APPROVED FOR THE DEPARTMENT OF PHYSICS

A handwritten signature in cursive script, reading "Joseph F. Becker", is written over a horizontal line.

Dr. Joseph F. Becker
Physics Department
San Jose State University

A handwritten signature in cursive script, reading "Patrick Hamill", is written over a horizontal line.

Dr. Patrick Hamill
Physics Department
San Jose State University

A handwritten signature in cursive script, reading "Carol R. Stoker", is written over a horizontal line.

Dr. Carol R. Stoker
Theoretical Studies Branch
NASA Ames Research Center

APPROVED FOR THE UNIVERSITY

A handwritten signature in cursive script, reading "Serene H. Stanford", is written over a horizontal line.

Abstract

The Destruction of Organic Compounds on Mars

Mark A. Bullock

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 H_2O_2 , 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 H_2O_2 distribution predicts that H_2O_2 cannot exist below depths of a meter. If H_2O_2 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.

Contents

1	Introduction	1
2	The Degradation of Organic Compounds Under Simulated Martian Conditions	4
2.1	Experimental Apparatus	4
2.2	Calibrations	6
2.2.1	Light Flux Calibration	6
2.2.2	Gas Chromatograph Calibration	7
2.3	Experimental Procedures	8
2.4	Data Analysis	9
2.5	Results	13
2.6	Discussion	14

3	Hydrogen Peroxide Transport on Mars	42
3.1	Introduction	42
3.2	Linear Soil Diffusion Model	46
3.2.1	Phase Partitioning	47
3.2.2	The Model	50
3.2.3	Results	52
3.2.4	Discussion	54
3.3	Nonlinear Soil Diffusion Model	59
3.3.1	Soil Diffusion Model	60
3.3.2	Numerical Results	62
3.3.3	Discussion	64
3.4	Coupled Soil/Atmosphere Model	68
3.4.1	The Model	71
3.4.2	Numerical Results	77
3.4.3	Discussion	81
3.5	Nonlinear Coupled Soil/Atmosphere Model	88

3.5.1	Introduction	88
3.5.2	The Model	94
3.5.3	Results	101
3.5.4	Discussion	103
3.6	Conclusions	110
4	References	112

List of Figures

2.1	Mars Jar	18
2.2	Mars Jars Gas Manifold	19
2.3	Mars Jars Experimental Apparatus	19
2.4	Mars Jars Sample Bulb	20
2.5	Perkin Elmer 900 Gas Chromatograph	20
2.6	UV Detector Calibration Curve	21
2.7	Visible Detector Calibration Curve	22
2.8	Xe Lamp Spectrum	23
2.9	Xe Lamp Flux Distribution	24
2.10	GC Hydrocarbon Standards Chromatogram	25
2.11	GC Sample Chromatogram	26
2.12	Hydrocarbon Production-High Flux Jar #1	27

2.13 Hydrocarbon Production–Low Flux Jar #2	28
2.14 Hydrocarbon Production–He Atmosphere Jar #3	29
2.15 Hydrocarbon Production–High Flux Jar #4	30
2.16 Hydrocarbon Production–He Atmosphere Jar #5	31
2.17 Hydrocarbon Production–Soil Only Jar #6	32
2.18 Hydrocarbon Production–High Flux Jar #7	33
2.19 Hydrocarbon Production–Low Flux Jar #8	34
2.20 Hydrocarbon Production–Glycine Only Jar #9	35
2.21 Hydrocarbon Production–Darkness Control #10	36
2.22 The Glycine Molecule	37
2.23 Mars Jars CH ₄ Production Rate vs. Flux	38
2.24 Mars Jars CH ₄ Photodegradation Quantum Efficiencies	39
3.1 H ₂ O ₂ Adsorption Isotherms	55
3.2 Density Case–Linear Soil Diffusion Model	56
3.3 Flux Case–Linear Soil Diffusion Model	57
3.4 Depth vs. Lifetime–Linear Soil Diffusion Model	58

3.5	Density Case–Nonlinear Soil Diffusion Model	66
3.6	Flux Case–Nonlinear Soil Diffusion Model	67
3.7	Density Case–Linear Coupled Model	83
3.8	Lifetime Case–Linear Coupled Model	84
3.9	H ₂ O ₂ Concentration vs. Lifetime–Linear Coupled Model	85
3.10	Depth vs. Lifetime–Linear Coupled Model	86
3.11	Atmospheric Concentration vs. Lifetime–Linear Coupled Model	87
3.12	Density Case–NonLinear Coupled Model	105
3.13	Lifetime Case–NonLinear Coupled Model	106
3.14	H ₂ O ₂ Concentration vs. Lifetime–NonLinear Coupled Model . .	107
3.15	Depth vs. Lifetime–NonLinear Coupled Model	108
3.16	Atmospheric Concentration vs Lifetime-NonLinear Coupled Model	109

List of Tables

2.1	Mars Jars and Controls	10
2.2	Mars Jars Quantum Efficiencies	15
2.3	GC Hydrocarbon Standards Spreadsheet	40
2.4	Mars Jars Data Analysis Spreadsheet	41
3.1	Hydrogen Peroxide Transport Models	45

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 5.2×10^{-5} and 6.9×10^{-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 CO₂ from the Viking Lander Labeled Release experiment (LR) is consistent with the presence of a thermally labile oxidant such as H₂O₂ (Klein 1979), which can act to destroy organics. H₂O₂ 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 O₂ 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 O₂ 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, H_2O_2 . 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 H_2O_2 production, transport and loss through the martian environment. If H_2O_2 is the oxidant responsible for the evolution of CO_2 in the LR experiment, we would like to predict to what depths it may exist. If there are depths below which H_2O_2 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 D₂ 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/ μ watts 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 phenylisocyanate 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.

Experiment	Mars Jar	Designation	Description
I	1	High Flux	soil + glycine + Mars gas
I	2	Low Flux	soil + glycine + Mars gas
I	3	He Atmosphere	soil + glycine + He
II	4	High Flux	soil + glycine + Mars gas
II	5	He Atmosphere	soil + glycine + He
II	6	Soil Only	soil + Mars gas
III	7	High Flux	soil + glycine + Mars gas
III	8	Low Flux	soil + glycine + Mars gas
III	9	Glycine Only	glycine + Mars gas
III	10	Darkness	soil + glycine + Mars gas

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
6. Calculations of the quantum efficiency.

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

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

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

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

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, $\overline{A}_{corr}$, given by

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

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_{MJ} , 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 1.73×10^{-6} CH₄/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 CH₄ production in the Mars simulations was 0.90×10^{-6} to 2.56×10^{-6} molecules/photon, based on the 2σ width of Figure 2.24. Higher order hydrocarbons, such as C₂H₆, C₂H₄, and C₃H₈ 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 CH₄ is catalytically

Mars Jar	Designation	Production nmoles/hr	Flux $\mu\text{W}/\text{cm}^2$	Q $\text{CH}_4/\text{photon}$
1	High Flux	0.255	201	1.49×10^{-6}
2	Low Flux	0.149	74.8	2.89×10^{-6}
3	He Atmosphere	0.069	27.0	4.94×10^{-6}
4	High Flux	0.205	155	1.56×10^{-6}
5	He Atmosphere	0.102	65.0	1.84×10^{-6}
6	Soil Only	0.027	26.4	0.37×10^{-6}
7	High Flux	0.124	117.3	1.27×10^{-6}
8	Low Flux	0.054	33.2	1.92×10^{-6}
9	Glycine Only	0.029	77.3	0.47×10^{-6}
10	Darkness	0.002		

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,

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

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 0.90×10^{-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:

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

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 $2.57 \mu\text{Watts cm}^{-2}$ (Kuhn and Atreya 1979). With flux levels of 27 to 201 $\mu\text{Watts cm}^{-2}$ 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

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

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

Figure 2.7 Visible Detector Calibration Curve

Figure 2.8 Xe Lamp Spectrum

Xe Lamp Flux Distribution 2000 - 2500 A $\mu\text{Watts}/\text{cm}^2$

Figure 2.9: Xe Lamp Flux Distribution

LIST: DEFO = 0. 0.14

RUN # 53

RT	AREA	TYPE	HR/HT	AREA%
1.63	4400200	SPB	0.051	11.260
2.38	8341300	SPB	0.076	21.344
2.95	8205800	TBP	0.102	20.998
4.55	1.2082E+07	TPV	0.137	30.916
5.87	6041800	TVB	0.275	15.460
9.66	8645	TBB	0.276	0.022

TOTAL AREA= 3.9080E+07
MUL FACTOR= 1.0000E+00

Figure 2.10: GC Hydrocarbon Standards Chromatogram

TOTAL AREA= 1767
MUL FACTOR= 1.0000E+00

HIGH FLUX 450HRS INJECTION 2

LIST: ZERO = 0. 0.08

LIST: ZERO = 0. 0.08

RUN # 89

RT	AREA	TYPE	HR/HT	AREA%
1.64	3426	VB	0.051	66.511
2.39	541	BP	0.065	10.503
2.95	1184	PP	0.133	22.986

TOTAL AREA= 5151
MUL FACTOR= 1.0000E+00

Figure 2.11: GC Sample Chromatogram

Figure 2.12 Hydrocarbon Production---High Flux Jar #1

Figure 2.13 Hydrocarbon Production---Low Flux Jar #2

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

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

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

	HYDROCARBON STANDARDS PERKIN ELMER 900				8/19/90
	PORASIL C	COLUMN	STANDARD C		
INJECTIONS	13,14,15,16		Ntotal (nmoles):		11057.49
INITIAL PRESSURE (torr):	759		TEMPERATURE (K):		295
VOLUME RATIO:	0.988		INJECTION VOLUME (cc):		0.268
	Acorr	s(%)	ni	MR	R
	counts		nmoles	counts/nmoles	
METHANE	5688979	0.12	22.11	257245	1.000
ETHANE	10483002	0.12	22.11	474023	1.843
ETHELYNE	10736532	0.78	22.11	485487	1.887
PROPANE	15922813	0.38	22.11	720001	2.799
ACETYLENE	7964453	0.61	22.11	360138	1.400

Table 2.3: GC Hydrocarbon Standards Spreadsheet

METHANE CONCENTRATIONS,				HIGH FLUX JAR		6/3/91	
BULB/GC RATIO:	0.481			METHANE M.R.	255591	counts/nmole	
JAR/MANIFOLD RATIO:	0.972			ETHANE M.R.	476756	counts/nmole	
MARS JAR VOLUME (cc)	345			ETHYLENE M.R.	475794	counts/nmole	
INJECTION VOLUME(cc)	0.268			TEMPERATURE	297	K	
DETECTOR 250 nm V/uW	15.85			DETECTOR 300 nm	18.3	Volts/uWatt	
MARS JAR AREA (cm2)	12.57						
EXTRACTION	TIME	Acorr	ns	Nmj	Nr	Nr(total)	N
	hours	counts	moles/cm	nmoles	nmoles	nmoles	nmoles
1	38	479	0.0070	2.484	0.0695	0.0695	2.484
2	87	3176	0.0464	16.456	0.4608	0.5303	16.525
3	159	4828	0.0705	25.017	0.7005	1.2308	25.547
4	232	6104	0.0891	31.627	0.8856	2.1163	32.858
5	349	8431	0.1231	43.689	1.2233	3.3396	45.805
6	450	9566	0.1397	49.568	1.3879	4.7275	52.908
7	542	12106	0.1767	62.731	1.7565	6.4840	67.459
8	808	15677	0.2289	81.233	2.2745	8.7585	87.717
EXTRACTION	TIME	Nprod	Ntot prod	N/hr	FLUX	INTENSITY	Q
	hours	nmoles	nmoles	nmoles/hr	Watts/cm	phot./sec	CH4/photon
1	38	2.484	2.484	0.0654	157	2.24E+16	4.89E-07
2	87	14.041	16.525	0.2866	124	1.77E+16	2.71E-06
3	159	9.022	25.547	0.1253	118	1.67E+16	1.25E-06
4	232	7.310	32.858	0.1001	108	1.53E+16	1.10E-06
5	349	12.948	45.805	0.1107	105	1.49E+16	1.24E-06
6	450	7.102	52.908	0.0703	133	1.9E+16	6.20E-07
7	542	14.551	67.459	0.1582	120	1.71E+16	1.55E-06
8	808	20.258	87.717	0.0762	73	1.04E+16	1.23E-06
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 H_2O_2 in Mars analog soils closely mimics the kinetics of the 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 superoxides 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 H_2O_2 is taken to be constant at all depths. The next model treats the partitioning between H_2O_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 H_2O_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 H_2O_2 in the atmosphere is considered, and a mass balance equation for the atmosphere is coupled with the soil diffusion equation. Thermal motion of H_2O_2 in the atmosphere and soil pore spaces allows molecules to be transported through the soil/atmosphere interface. The net flux of H_2O_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 *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.

	Uncoupled Soil Diffusion Models	Coupled Soil/Atmosphere Models
Linear	Section 3.2 Linear Soil Diffusion Model	Section 3.4 Coupled Soil/Atmosphere Model
Nonlinear	Section 3.3 Nonlinear Soil Diffusion Model	Section 3.5 Nonlinear Coupled Soil Atmosphere Model

Table 3.1: Hydrogen Peroxide Transport Models

3.2 Linear Soil Diffusion Model

In order to understand the distribution of H_2O_2 in the martian soil, a simple model based upon the diffusion of H_2O_2 through a permeable soil is developed. It is assumed that H_2O_2 produced in the martian atmosphere is in some way transferred to the soil surface. The H_2O_2 then diffuses downwards. It is further assumed that some fraction of the H_2O_2 is adsorbed onto the soil grains, and that the adsorbed H_2O_2 undergoes heterogenous catalytic destruction. The ratio of vapor phase to adsorbed phase H_2O_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, τ , against catalytic destruction. This first order model ignores the question of how H_2O_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, $30 \text{ nmoles cm}^{-3}$ (Klein 1978). The lifetime of H_2O_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 3.15×10^{12} seconds.
2. **Flux Case** – The flux into the soil is taken to be identical with the odd hydrogen production rate (Hunten 1979), $4 \times 10^9 \text{ cm}^{-2} \text{ sec}^{-1}$. The lifetime of H_2O_2 in this case is assumed to be one terrestrial year, or 3.15×10^7

seconds.

3.2.1 Phase Partitioning

At martian temperatures and pressures, H_2O_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 H_2O onto clean basalt surfaces for concentrations several orders of magnitude higher than those expected for H_2O_2 adsorbed onto martian soil grains. Nevertheless, since H_2O_2 has a dipole moment and vapor pressure curve similar to H_2O , the Fanale and Cannon isotherms will be used as a starting point to estimate H_2O_2 phase partitioning under martian conditions. The adsorption data are represented by an expression that gives the number of grams of H_2O_2 adsorbed per gram of soil, as a function of temperature and partial pressure. The expression is

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

where:

R_a = grams of adsorbed H_2O_2 per gram of soil

P = partial pressure of H_2O_2

T = 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 ρ_{soil} are the densities of the adsorbed H_2O_2 and soil, respectively.

If μ 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

$$P = \frac{n_v}{N_o} RT$$

so

$$\frac{n_c \mu_{H_2O_2}}{N_o \rho_{soil}} = \frac{A_o}{C_o^{0.51}} \left(\frac{n_v}{N_o} RT \right)^{0.51} e^{-\frac{E_o D_o}{T}}$$

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

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

$$n_c(z) = S(T) n_v^{\frac{1}{2}}(z) \quad (3.1)$$

where:

$$S(T) = \frac{\rho_{soil} A_o N_o}{C_o^{0.51} \mu_{H_2O_2}} \left(\frac{RT}{N_o} \right)^{0.51} e^{-\frac{E_o D_o}{T}}$$

For this isothermal model, an average martian surface temperature of 215 K is used. Isotherms for several temperatures are shown in 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_2O_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_2O_2 in a volume cell depends upon the porosity of the soil, ϵ . This is the ratio of the interstitial pore space volume to total volume. The catalytic destruction of H_2O_2 is characterized by its lifetime in the soil, τ . If D , then, is the diffusion coefficient for H_2O_2 , the diffusion equation is

$$\epsilon \frac{\partial n_v(z, t)}{\partial t} + \frac{\partial n_c(z, t)}{\partial t} = Df \frac{\partial^2 n_c(z, t)}{\partial z^2} - \frac{n_c(z, t)}{\tau} \quad (3.2)$$

where $n_c(z, t)$ is the concentration of adsorbed H_2O_2 and $n_v(z, t)$ is the concentration of vapor phase H_2O_2 in the soil pore spaces. Considering the limit to steady state,

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

The steady state soil equation is:

$$\frac{\partial^2 n_c(z)}{\partial z^2} - \frac{1}{D\tau f} n_c(z) = 0 \quad (3.3)$$

Density Case

The boundary conditions for this case are:

BC 1

$$\lim_{z \rightarrow \infty} n_c(z) = 0$$

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,

$$\lim_{z \rightarrow \infty} n_c(z) = 0$$

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 $\frac{1}{e}$ folding depth of

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

Flux Case

The boundary conditions for this case are:

BC 1

$$\lim_{z \rightarrow \infty} n_c(z) = 0$$

which is the same as for the Density Case, and

BC 2

$$-D \left. \frac{\partial n_v(z)}{\partial z} \right|_{z=0} = F_i$$

where F_i is the flux of H_2O_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 $n_c(z)$,

$$\begin{aligned} -Df \left. \frac{\partial n_c(z)}{\partial z} \right|_{z=0} &= F_i \\ \frac{Df n_c(0)}{(D\tau f)^{\frac{1}{2}}} &= F_i \end{aligned}$$

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:

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

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

$$f = 8 \times 10^{-10}$$

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

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

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

H₂O₂ 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:

$$n_c(0) = 10,324 \text{ nmoles cm}^{-3}$$

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

$$\delta = 0.02 \text{ cm}$$

H₂O₂ concentration vs. depth for the Flux Case is plotted in Figure 3.3. The lifetime of H₂O₂ 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_2O_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_2O_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_2O_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_2O_2 in the soil.

Figure 3.1 H_2O_2 Adsorption Isotherms

Figure 3.2 Density Case -- Linear Soil Diffusion Model

Figure 3.3 Flux Case --- Linear Soil Diffusion Model

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_2O_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_2O_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_2O_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_2O_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:

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

With boundary conditions:

BC 1

$$\lim_{z \rightarrow \text{large}} \frac{\partial n_v(z, t)}{\partial z} = 0$$

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,

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

The steady state soil diffusion equation is then

$$\frac{d^2 n_v(z)}{dz^2} - \frac{n_c(z)}{D\tau} = 0 \tag{3.6}$$

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

$$\frac{d^2 n_v(z)}{dz^2} = \frac{S}{D\tau} n_v^{\frac{1}{2}}(z) \tag{3.7}$$

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 H_2O_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

$$n_c(z) = S n_v^{\frac{1}{2}}(z)$$

the adsorbed phase concentration is

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

Applying **BC 2 – Density Case**

At $z = 0$,

$$\begin{aligned} n_c(0) &= S C_2^2 \\ C_2 &= \frac{n_c^{\frac{1}{2}}(0)}{S^{\frac{1}{2}}} \end{aligned}$$

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

$$n_c(z) = \left[n_c^{\frac{1}{2}}(0) - \frac{1}{2\sqrt{3}} \frac{S}{(D\tau)^{\frac{1}{2}}} z \right]^2 \quad (3.8)$$

Applying **BC 2 – Flux Case**

$$\begin{aligned} \frac{dn_v}{dz} &= 4 \left[C_2 - \frac{1}{2\sqrt{3}} \left(\frac{S}{D\tau} \right)^{\frac{1}{2}} z \right]^3 \left[-\frac{1}{2\sqrt{3}} \left(\frac{S}{D\tau} \right)^{\frac{1}{2}} \right] \\ -D \frac{dn_v}{dz} \Big|_{z=0} &= 4 C_2^3 D \frac{1}{2\sqrt{3}} \left(\frac{S}{D\tau} \right)^{\frac{1}{2}} = F_i \end{aligned}$$

$$C_2 = \left(\frac{F_i}{2}\right)^{\frac{1}{3}} \left(\frac{3\tau}{DS}\right)^{\frac{1}{6}}$$

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

$$n_c(z) = \left[\left(\frac{SF_i}{2}\right)^{\frac{1}{3}} \left(\frac{3\tau}{D}\right)^{\frac{1}{6}} - \frac{1}{2\sqrt{3}} \frac{S}{(D\tau)^{\frac{1}{2}}} z \right]^2 \quad (3.9)$$

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_2O_2 concentration and destruction and diffusion parameters,

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

or, the surface concentration may be expressed in terms of the flux of H_2O_2 into the soil and destruction and diffusion parameters,

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

3.3.2 Numerical Results

Density Case

For the Density Case, the adsorbed H_2O_2 concentration is constrained, and the solution to the soil diffusion equation is given by Equation 3.8,

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

The concentration of adsorbed H_2O_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,

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

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

$$\tau = 3.15 \times 10^{12} \text{ sec}^{-1}$$

$$S = 4.737 \times 10^{12} \text{ cm}^{-\frac{3}{2}}$$

the extinction depth is calculated to be:

$$z_e = 22.246 \text{ cm}$$

The flux of H_2O_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_2O_2 into the soil is given, the solution to the soil diffusion equation is given by Equation 3.9,

$$n_c(z) = \left[\left(\frac{SF_i}{2} \right)^{\frac{1}{3}} \left(\frac{3\tau}{D} \right)^{\frac{1}{6}} - \frac{1}{2\sqrt{3}} \frac{S}{(D\tau)^{\frac{1}{2}}} z \right]^2$$

The concentration of adsorbed H_2O_2 goes to zero at a finite depth, z_e , given by:

$$z_e = \left(\frac{36F_i D \tau^2}{S^2} \right)^{\frac{1}{3}}$$

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 H_2O_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 H_2O_2 at all. This is caused by the nonlinear nature of the soil diffusion equation. The greater the depth, the less vapor phase H_2O_2 there is, and the less vapor phase H_2O_2 there is, the more adsorbed phase H_2O_2 there is in proportion to it. Since there is a higher proportion of adsorbed H_2O_2 at greater depth, there is more H_2O_2 available, proportionally, to be destroyed. This results in a positive feedback that destroys H_2O_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_2O_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_2O_2 enters the soil at the same rate it is produced in the atmosphere, the extinction depth for H_2O_2 is even smaller, 0.4 cm, and the surface concentration of H_2O_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 H_2O_2 into the soil, in this section a simple model that couples the creation, transport and destruction of H_2O_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 H_2O_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 H_2O_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 H_2O_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. H_2O_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_2O_2 is deposited into the soil by the thermal motion of molecules at the surface.
4. H_2O_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_2O_2 is physically adsorbed on the surface of the soil grains, and that vapor phase H_2O_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_2O_2 and $n_c(z)$ is the adsorbed phase number density of H_2O_2 . This treatment of the phase partitioning is the same as in section 3.2.

5. The transport of H_2O_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_2O_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 $D_K = \frac{4}{9} \frac{e r_p}{\tau^2} \left[\frac{2kT}{\pi m} \right]$, and has a value under these conditions of $D_K = 0.0163 \text{ cm}^2 \text{ sec}^{-1}$.
6. Since vapor phase H_2O_2 at the surface of the soil is free to reenter the atmosphere, the assumption is made that the thermal motion of H_2O_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, τ . 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 $30 \text{ nmoles cm}^{-3}$ (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 $3.15 \times 10^{12} \text{ sec}$.

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_2O_2 molecules

P is the column production rate

l is the loss rate of H_2O_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:

$c = \sqrt{\frac{8kT}{\pi m}}$, the average molecular speed at 215 K.

At martian surface temperatures, H_2O_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_2O_2 out of the soil and into the atmosphere column. The concentration of adsorbed phase H_2O_2 is denoted as $n_c(z)$, and the number density of the vapor phase is $n_v(z)$. Then the flux of H_2O_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,

$$F_o = \frac{1}{4}cf n_c(0)$$

The conservation equation for H_2O_2 in the martian atmosphere becomes:

$$\frac{dN_a(t)}{dt} = P - lN_a(t) - \frac{\frac{1}{4}cN_a(t)}{H} + \frac{1}{4}cf n_c(0)$$

Since it is the long term equilibrium distribution of H_2O_2 that is of interest, this equation is solved for the steady state,

$$\lim_{t \rightarrow \infty} \frac{dN_a(t)}{dt} = 0 \quad \text{and} \quad \lim_{t \rightarrow \infty} N_a(t) = N_a$$

and the atmosphere equation becomes

$$P - lN_a - \frac{\frac{1}{4}cN_a}{H} + \frac{1}{4}cf n_c(0) = 0$$

For the purposes of coupling this equation to the equation describing H_2O_2 transport through the soil, concentrations are expressed in terms of number densities. Thus,

$$P - lHn_a(0) - \frac{1}{4}cn_a(0) + \frac{1}{4}cf n_c(0) = 0 \quad (3.13)$$

solving for $n_a(0)$,

$$\begin{aligned} (lH + \frac{1}{4}c)n_a(0) &= P + \frac{1}{4}cf n_c(0) \\ n_a(0) &= \frac{P + \frac{1}{4}cf n_c(0)}{lH + \frac{1}{4}c} \end{aligned} \quad (3.14)$$

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 $n_c(z) = \frac{1}{f}n_v(z)$.

In order to calculate the adsorbed H_2O_2 concentration as a function of depth, it is necessary to model the diffusion and destruction of H_2O_2 through the soil, with boundary conditions consistent with the atmosphere model. It is known that H_2O_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_2O_2 has been adsorbed onto the iron rich soil grains. In this model, the destruction rate is expressed in terms of a lifetime, τ , so that the destruction rate of H_2O_2 in the soil is given by

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

The diffusion equation for H_2O_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:

ϵ is the porosity of the soil.

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

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

where:

D is the diffusion coefficient.

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

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

which is subject to the boundary conditions,

BC 1

$$\lim_{z \rightarrow \infty} n_c(z, t) = 0$$

BC 2

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

or,

$$-Df \left. \frac{\partial n_c(z, t)}{\partial z} \right|_{z=0} = \frac{1}{4}cn_a(0) - \frac{1}{4}cf n_c(0)$$

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,

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

The steady state soil equation is then

$$\frac{\partial^2 n_c(z)}{\partial z^2} - \frac{1}{D\tau f} n_c(z) = 0 \tag{3.16}$$

Solutions have the form

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

Applying BC 1,

$$\lim_{z \rightarrow \infty} n_c(z) = 0$$

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,

$$-Df \left. \frac{\partial n_c(z, t)}{\partial z} \right|_{z=0} = \frac{1}{4}cn_a(0) - \frac{1}{4}cf n_c(0)$$

This is solved for $n_c(0)$.

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

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 $n_c(0)$:

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

From this, the concentration of H_2O_2 in the soil at any depth may be calculated from the solution to the soil diffusion Equation 3.17. The $\frac{1}{e}$ folding depth may be found in the exponent, and is

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

For the density case, the average concentration in the top 4 cm is specified. If this concentration is denoted as n_l , and the depth to which the concentration is averaged is z_l ,

$$n_l = \frac{1}{z_l} \int_0^{z_l} n(z) dz$$

or

$$n_l = n_c(0) \frac{\delta}{z_l} \left[1 - e^{-\frac{z_l}{\delta}} \right] \quad (3.21)$$

For $z_l \gg \delta$,

$$n_c(0) = \frac{n_l z_l}{(D\tau f)^{\frac{1}{2}}}$$

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

$$n_c(0) = \frac{\sqrt{(n_l z_l l H f)^2 + 4 P D f n_l z_l \left[\frac{4 l H}{c} + 1 \right]} - n_l z_l l H f}{2 D f \left[\frac{4 l H}{c} + 1 \right]} \quad (3.22)$$

Equation 3.19 may also be rearranged to obtain an expression for the lifetime of H_2O_2 in the soil,

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

The concentration of H_2O_2 in the atmosphere at the surface may be calculated from Equation 3.14,

$$n_a(0) = \frac{P + \frac{1}{4} c f n_c(0)}{l H + \frac{1}{4} c}$$

For the lifetime case, $n_c(0)$ and δ are calculated directly from Equations 3.19 and 3.20, and the average concentration of H_2O_2 in the top layer of soil is calculated from equation 3.21.

3.4.2 Numerical Results

Density Case

For the density case, τ is treated as a free parameter, and the average surface soil concentration is constrained to be $30 \text{ nmoles cm}^{-3}$. To calculate the lifetime, τ , the characteristic depth, δ , 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 H_2O_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 H_2O_2 in the pores spaces of the soil. Since $n_v(0) = fn_c(0)$,

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

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

$$\text{Atmospheric production flux } 4.183 \times 10^{10} \text{ cm}^2 \text{ sec}^{-1}$$

$$\text{Atmospheric loss flux } 4.159 \times 10^{10} \text{ cm}^2 \text{ sec}^{-1}$$

$$\text{Flux into the soil } 8.452 \times 10^{12} \text{ cm}^2 \text{ sec}^{-1}$$

$$\text{Flux out of the soil } 8.452 \times 10^{12} \text{ cm}^2 \text{ sec}^{-1}$$

$$\text{Diffusion/destruction flux } 2.402 \times 10^8 \text{ cm}^2 \text{ sec}^{-1}$$

where the diffusion/destruction flux is given by

$$F_d = \left(\frac{D}{\tau f} \right)^{\frac{1}{2}} n_v(0) = \left(\frac{D}{\tau f} \right)^{\frac{1}{2}} fn_c(0) \quad (3.24)$$

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 H_2O_2 to the surface to account for the Viking LR experiment results. Figure 3.7 shows the exponential depth profile of H_2O_2 for the density case.

Lifetime Case

For the lifetime case, the concentration of H_2O_2 at the surface is treated as a free parameter, and the lifetime against catalytic destruction is 3.15×10^{12} seconds. To calculate the characteristic depth, τ , 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 H_2O_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 H_2O_2 in the pore space of the soil. Since $n_v(0) = fn_c(0)$,

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

Calculating the fluxes involved for the lifetime case,

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

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

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

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

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

where the diffusion/destruction flux is again given by

$$F_d = \left(\frac{D}{\tau f} \right)^{\frac{1}{2}} n_v(0) = \left(\frac{D}{\tau f} \right)^{\frac{1}{2}} fn_c(0) \quad (3.25)$$

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 H_2O_2 , since the soil is virtually passive. Since the gradient at the soil surface is not strong, the vapor phase concentration of H_2O_2 in the pore spaces is nearly

the same as the atmospheric concentration. Through the phase partitioning relation, $f = \frac{n_v(0)}{n_c(0)}$, the concentration of adsorbed H_2O_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 H_2O_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 H_2O_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 H_2O_2 adsorbed at the surface is assumed to be 30 nmoles cm^{-3} , the model predicts a H_2O_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 H_2O_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 H_2O_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 H_2O_2 as an explanation of the Viking LR experiment results. Furthermore, if 10^5 years is considered as an upper bound for H_2O_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 H_2O_2 is the primary oxidant in the martian soil, destruction of organic material may cease at depths approaching a meter.

Figure 3.7 Density Case --- Linear Coupled Model

Figure 3.8 Lifetime Case --- Linear Coupled Model

Figure 3.9 H_2O_2 Concentration vs. Lifetime --- Linear Coupled Model

Figure 3.10 Depth vs. Lifetime --- Linear Coupled Model

Figure 3.11 Atmospheric Concentration vs. Lifetime --- 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_2O_2 through the martian soil and atmosphere have incorporated either an ad hoc soil/atmosphere coupling or have ignored the division of H_2O_2 into adsorbed and vapor phases. Presented here is an analytical model that predicts atmospheric and soil concentrations of H_2O_2 based on a net flux of H_2O_2 into the soil and on adapting empirically derived adsorption isotherms for water 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_2O_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_2O_2 into the soil is established by the atmospheric concentration at the surface as well as by soil diffusion and loss processes. Similarly, atmospheric concentrations are dependent upon both atmospheric and soil processes.

In order to uniquely determine a solution, the model requires that atmospheric production and loss rates, as well as soil loss and diffusion rates, be known.

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

Atmospheric Production

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

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

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

Using a value of $6.5 \times 10^7 \text{ cm}^{-3}$ 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_2O_2 is

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

Atmospheric Loss

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

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.

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

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

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_2O_2 onto grain surfaces, and by the subsequent catalytic destruction of the adsorbed phase. Diffusion of a gas through porous media may be modeled by two different mechanisms depending on whether the mean free path of the gas is greater or less than the average pore diameter. If pores are mostly larger than the mean free path, diffusion is dominated by molecular collisions. In this case, the diffusion coefficient is the gas-gas diffusion coefficient of H_2O_2 in CO_2 multiplied by a constant that depends upon

the geometry of the soil. This transport mechanism is referred to as molecular diffusion. An analytical expression for the diffusion coefficient is obtained by modeling the pores in the soil as randomly twisted and distributed tubes embedded in a cross section of the soil (Ball 1981). Porosity is defined as the ratio of the 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 $D_m = \frac{\epsilon}{\tau^2} D_o$ where D_o is the gas-gas diffusion coefficient, ϵ is the soil porosity, and τ is the soil tortuosity (Flood 1967). The value of the molecular diffusion coefficient for H_2O_2 in CO_2 at an average surface temperature of 215 K is $D_m = 0.678 \text{ cm}^2 \text{ sec}^{-1}$.

If pores are mostly smaller than the mean free path, molecular collisions with the pore walls dominate the transport of H_2O_2 a process known as Knudsen diffusion. The average pore size may be taken to be $1 \text{ } \mu\text{m}$ (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 $27.8 \text{ } \mu\text{m}$. Therefore, Knudsen diffusion is the dominant transport mechanism for H_2O_2 through the martian soil at this temperature. The Knudsen diffusion coefficient is given analytically as $D_K = \frac{4}{9} \frac{\epsilon r_o}{\tau^2} \left[\frac{2kT}{\pi m} \right]$ where r_o is the average pore radius and m is the H_2O_2 molecular mass (Fanale *et al.*, 1986). The value of the Knudsen diffusion coefficient for H_2O_2 in the martian soil is calculated to be $D_K = 0.0163 \text{ cm}^2 \text{ sec}^{-1}$.

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_2O_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_2O_2 under martian conditions are poorly constrained. The model is solved for a wide range of lifetimes in order to assess the sensitivity of soil concentrations and atmospheric losses to differences in soil lifetimes.

Phase Partitioning

Empirically derived isotherms for the adsorption of H_2O in the martian soil yield a power law relationship between adsorbed and vapor phases. The vapor pressure curves for H_2O and H_2O_2 are fairly similar at low temperatures, as are the molecular dipole moments. However, the concentrations of H_2O in the martian soil are much higher than those of H_2O_2 and it should be expected that there is some variation in the adsorption isotherms between H_2O and H_2O_2 . Since specific laboratory data on the adsorption of H_2O_2 under martian conditions is lacking, the isotherms for H_2O are used to describe the phase partitioning for H_2O_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

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

For a soil that is a poor atmospheric sink, the amount of adsorbed H_2O_2 may be estimated, assuming that H_2O_2 in the soil pore spaces is in pressure equilibrium with the atmosphere.

$$n_c = S(T)n_v^{\frac{1}{2}} = 240 \text{ nanomoles cm}^{-3}$$

This represents a maximum amount of H_2O_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 H_2O_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

H₂O₂ under such constraints. The model is solved in the Lifetime case for a lifetime of 10⁵ years. By considering the adsorbed H₂O₂ 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 H₂O₂ is calculated. The third case examined is the Loss Regime Case. If H₂O₂ 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 H₂O₂. 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 H₂O₂ enters in the soil equation.

The Atmosphere Equation

If N_a is the column density of H₂O₂ in the martian atmosphere,

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

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 H_2O_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 H_2O_2 that is of interest, this equation is solved for the steady state

$$\lim_{t \rightarrow \infty} \frac{\partial n_a(z, t)}{\partial t} = 0 \quad \text{and} \quad \lim_{t \rightarrow \infty} n_a(0, t) = n_a(0)$$

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 H_2O_2 in the pore spaces near the surface.

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

With these substitutions, the atmosphere equation becomes

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

Solving for the atmospheric concentration at the surface,

$$n_a(0) = \frac{P + \frac{1}{4}cn_v(0)}{lH + \frac{1}{4}c} \quad (3.28)$$

The Soil Diffusion Equation

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

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

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

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

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

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

Again, the steady state solution is sought,

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

The steady state isothermal soil diffusion equation becomes

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

with boundary conditions

BC 1

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

BC 2

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

where the flux boundary condition couples to the atmosphere equation through

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

The nonlinear soil diffusion 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:

$$\frac{dn_v}{dz} = \pm \frac{2}{\sqrt{3}} \left(\frac{S}{D\tau} \right)^{\frac{1}{2}} n_v^{\frac{3}{4}} \quad (3.31)$$

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 $n_v^{\frac{1}{4}}(0)$ and must be determined from the second boundary condition. Since the quantity of interest is the concentration of adsorbed H_2O_2 , the phase partitioning function derived in Section 3.2.1 is used.

$$n_c = S n_v^{\frac{1}{2}}$$

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,

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

Then the net flux of H_2O_2 into the soil is, by the second boundary condition,

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

in terms of atmospheric production and loss terms,

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

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

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

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

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

Again, since it is the concentration of adsorbed H_2O_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 $n_c(0)$,

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

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_2O_2 in the soil is given by the general solution, Equation 3.32. Other physically significant quantities may also be calculated from $n_c(0)$.

Extinction Depth The general solution to the soil diffusion equation, equation 3.32, shows that the concentration of adsorbed H_2O_2 goes to zero at a finite depth. Due to the nonlinear phase partitioning, $n_c = S(T)n_v^{\frac{1}{2}}$, as the concentration of mobile H_2O_2 decreases with depth, the concentration of adsorbed H_2O_2 decreases at the square of this rate. The result is a rapid decrease in adsorbed H_2O_2 with depth. The solution,

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

goes to zero at a finite depth, z_e . For $n_c(z_e) = 0$,

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

So that the extinction depth is

$$z_e = \left(\frac{12D\tau}{S^2} \right)^{\frac{1}{2}} n_c^{\frac{1}{2}}(0) \quad (3.34)$$

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

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

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

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

Performing the integration,

$$n_l = \begin{cases} \frac{2}{z_l} \left[n_c^{\frac{1}{2}}(0) - \left(\frac{S^2}{12D\tau} \right)^{\frac{1}{2}} z \right]^3 \left(-\frac{S^2}{12D\tau} \right)^{\frac{1}{2}} \Big|_0^{z_l} & z_l < z_e \\ \frac{2}{z_l} \left[n_c^{\frac{1}{2}}(0) - \left(\frac{S^2}{12D\tau} \right)^{\frac{1}{2}} z \right]^3 \left(-\frac{S^2}{12D\tau} \right)^{\frac{1}{2}} \Big|_0^{z_e} & z_l \geq z_e \end{cases}$$

The average concentration of adsorbed H_2O_2 in the top 4 cm of soil is

$$n_l = \begin{cases} \left(\frac{4D\tau}{3S^2} \right)^{\frac{1}{2}} \frac{n_c^{\frac{3}{2}}(0)}{z_l} & z_l < z_e \\ \left(\frac{4D\tau}{3S^2} \right)^{\frac{1}{2}} \frac{n_c^{\frac{3}{2}}(0)}{z_l} \left[\left(\frac{z_l}{z_e} - 1 \right)^3 + 1 \right] & z_l \geq z_e \end{cases} \quad (3.35)$$

Atmospheric Number Density Equation 3.28 for the atmospheric number density at the surface may be expressed in terms of the H_2O_2 adsorbed phase concentration in the soil via the phase partitioning function

$$n_a(0) = \frac{P + \frac{1}{4} \frac{c}{S^2} n_c^2(0)}{lH + \frac{1}{4}c} \quad (3.36)$$

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,

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

Once again, this quantity may be expressed in terms of the adsorbed phase concentration of H_2O_2 through the phase partitioning function

$$F_{soil} = \left(\frac{4D}{3\tau S^2} \right)^{\frac{1}{2}} n_c^{\frac{3}{2}}(0) \quad (3.37)$$

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 H_2O_2 into the soil, in terms of the soil lifetime parameter.

3.5.3 Results

Density Case

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

$$\tau = 1.79 \times 10^9 \text{ sec} \simeq 57 \text{ terrestrial years}$$

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 H_2O_2

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

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

Lifetime Case

Assuming H_2O_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 H_2O_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 $240 \text{ nmoles cm}^{-3}$, 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 H_2O_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_2O_2 . By identifying these regimes, it is possible to assess the effect of assumptions about the lower boundary condition used in more complex atmospheric models. In the Loss Regime Case, the physical quantities are calculated for the condition that the soil and atmosphere are H_2O_2 sinks of equal magnitude. This condition is met when the lifetime of H_2O_2 in the soil is

$$\tau = 40 \text{ minutes}$$

The resulting average surface concentration is very small,

$$n_l = 0.002 \text{ nmoles cm}^{-3}$$

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_2O_2 that is comparable with the atmosphere, surface concentrations will be extremely small, with all the H_2O_2 residing very close to the surface.

3.5.4 Discussion

The nonlinear relationship between adsorbed and vapor phase H_2O_2 results in a parabolic depth profile for the solution to the soil diffusion equation. This curious result implies that H_2O_2 is actually extinguished at a finite depth, rather than asymptotically approaching zero, as for a linear diffusion equation. Depth profiles for the Density and Lifetimes Cases are shown in 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 H_2O_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 H_2O_2 in the top 4 cm of soil, the extinction depth, and the atmospheric number density at the surface. These quantities are plotted as a function of the lifetime parameter in Figures 3.14, 3.15 and 3.16.

Figure 3.12 Density Case --- Nonlinear Coupled Model

Figure 3.13 Lifetime Case --- Nonlinear Coupled Model

Figure 3.14 H_2O_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 $30 \text{ nmoles cm}^{-3}$. 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_2O_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_2O_2 . Therefore, atmospheric concentrations of H_2O_2 predicted by this model are consistent with more complex atmospheric models that assume a passive surface. It may be concluded that as long as the lifetime of H_2O_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_2O_2 in the soil that is consistent with the Viking Biology experiment results, the soil is a poor sink for H_2O_2 compared with the atmosphere. Unless the lifetime is on the order of an hour or less, the atmosphere may be considered the primary sink for H_2O_2 . Given this condition, more complex models of H_2O_2 production and loss in the martian atmosphere that neglect losses to the soil do so without loss of accuracy. For all lifetimes shorter than 10^5 years, the depth to complete extinction of H_2O_2 was less than 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_2O_2 may penetrate. If H_2O_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, *J. Mole. Evol.* **14**, 33-38, 1979.
- Ball, B. C., Modeling of Soil Pores as Tubes Using Gas Permeabilities, Gas Diffusivities and Water Release, *J. Soil Sci.* **32**, 465-481, 1981.
- 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**, 644-645, 1978.
- 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 Presence and Role in Viking Biology Experimental Results. *J. Mole. Evol.*

14, 133-152, 1979.

Banin, A., G.C. Carle, S. Chang, L.M. Coyne, J.B. Ohrenberg and T. Scattergood, Laboratory Investigations of Mars: Chemical and Spectroscopic Characteristics of a Suite of Clays as Mars Soil Analogs. *Origins of Life* 18, 239-265, 1988.

Biemann, K., J. Oro, P. Toulmin, III, L.E. Orgel, A.O. Nier, D.M. Anderson, P.G. Simmonds, D. Flory, A.V. Diaz, D.R. Rushneck, J.E. Biller, and A.L. LaFleur, The Search for Organic Substances and Inorganic Volatile Compounds in the Surface of Mars. *J. Geophys. Res.* 82, 4641-4658, 1977.

Biemann, K., The Implications and Limitations of the Findings of the Viking Organic Analysis Experiment, *J. Mole. Evol.* 14, 65-70, 1979.

Biemann, K., and J.M. Lavoie, Some Final Conclusions and Supporting Experiments Related to the Search for Organic Compounds on the Surface of Mars, *J. Geophys. Res.* 84, 8385-8390, 1979

Blackburn, T.R., H.D. Holland and G.P. Ceasar, Viking Gas Exchange Reaction: Simulation on UV-Irradiated Manganese Dioxide Substrate, *J. Geophys. Res.* 84, 8391-8394, 1979.

Chun, S.F.S., K.D. Pang, J.A. Cutts, J.M. Ajello, Photocatalytic Oxidation of Organic Compounds on Mars, *Nature* 274, 875-876, 1978.

Chyba, C., S.W. Squyres and C. Sagan, Lunar and Planetary Science XX, 157-158, 1989.

- DeMore, W.B., ed., *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation 7*, JPL Pub. 85-37, 217 pp., 1985.
- Fanale, F. P., W. A. Cannon, Adsorption on the Martian Regolith, *Nature* **230**, 502 - 504, 1971.
- Fanale, F.P., J.R. Salvail, W.B. Banerdt and R.S. Saunders, The Regolith-Atmosphere-Cap System and Climate change, *Icarus* **50**, 381-407, 1982.
- Fanale, F.P., J.R. Salvail, A.P. Zent and S.E. Postawko, Global Distribution and Migration of Subsurface Ice on Mars, *Icarus* **67**, 1-18, 1986.
- Fanale, F.P., Comments on the Potential Hazards of Peroxides and Superoxides in Mars Soil, in Study of Martian Surface and Atmospheric Effects on Mars Rover, Lander and Balloons, *JPL Tech Rep. D4657*, pp. 4.2-4.5, 1987.
- Farmer, C. B., P. E. Doms, Global and Seasonal Variations of Water Vapor on Mars the Implications for Permafrost, *J. Geophys. Res.* **84**, 2881 - 2888, 1977.
- Flood, E.A., ed., *The Solid Gas Interface*, Marcel Dekker, Inc., New York, 1967.
- Flynn, G. J. and D.S. McKay, An Assesment of the Meteoritic Contribution to the Martian Dust, submitted *J. Geophys. Res.*, 1989.
- Hubbard, J.S., The Pyrolitic Release Experiment: Measurement of Carbon Assimilation, *Origins of Life* **7**, 281-292, 1976.
- Hubbard, J.S., Laboratory Simulations of the Pyrolitic Release Experiments: an Interim Report, *J. Mol. Evol.* **14**, 211-221, 1979.

-
- Huguenin, R.L., The Formation of Goethite and Hydrated Clay Minerals on Mars, *J. Geophys. Res.* **79**, 3895-3904, 1974
- Huguenin, R.L., K.J. Miller, and W.S. Harwood, Frost-Weathering on Mars: Experimental Evidence for Peroxide Formation. *J. Mole. Evol.* **14**, 103-132, 1979.
- Huguenin, R.L., Chemical Weathering and the Viking Biology Experiments on Mars, *J. Geophys. Res.* **87**, 10069-10082, 1982.
- Hunten, D.M., Aeronomy of the Lower Atmosphere of Mars, *Rev. Geophys. Space Phys.* **12**, 529-535, 1974.
- Hunten, D., Possible Oxidant Sources in the Atmosphere and Surface of Mars, *J. Mol. Evol.* **14**, 57-64, 1979.
- Hunten, D.M., Oxidants in the Martian Atmosphere and Soil, in Study of Martian Surface and Atmospheric Effects on Mars Rover, Lander and Ballons, *JPL Tech. Rep, D-4657* pp. 4.7-4.13, 1987.
- Klein, H.P., N.M Horowitz, G.V. Levin, V.I. Oyama, J. Lederberg, A. Rich, J.S. Hubbard, G.L. Hobby, P.A. Straat, B.J. Berdahl, G.C. Carle, F.S. Brown, R.D. Johnson, The Viking Biological Investigation: Preliminary Results, *Science* **194**, 1976.
- Klein, H.P., The Viking Biological Experiments on Mars. *Icarus* **34**, 666- 674, 1978.
- Klein, H.P., The Viking Mission and the Search for Life on Mars, *Rev. Geophys.*

- and Space Phys.* **17**, 1655-1662, 1979.
- Klein, H.P., Simulation of the Viking Biology Experiments: An Overview, *J. Mol. Evo.* **14**, 161-165, 1979.
- Klein, H.P., The Search for Life on Mars, in The Surface of Mars, 190, Yale Univ. Press., 1981.
- Kong, T.Y. and M.B. McElroy, Photochemistry of the Martian Atmosphere, *Icarus* **32**, 168-189, 1977.
- Kong, T.Y., and M.B. McElroy, The Global Distribution of O₃ on Mars, *Planet. Space Sci.* **25**, 839-857, 1977.
- Kuhn, W.R. and S.K. Atreya, Solar Radiation Incident on the Martian Surface, *J. Mol. Evol.* **14**, 57-64, 1979.
- Levin, G.V. and P.A. Straat, Recent Results from the Viking Labeled Release Experiment on Mars. *J. Geophys. Res.* **82**, 4663-4667, 1977.
- Levin, G.V. and P.A. Straat, *J. Mol. Evol.*, **14**, 167-183, 1979.
- Levin, G.V. and P.A. Straat, A Search for Nonbiological Explanation of the Viking Labeled Release Life Detection Experiment, *Icarus* **45**, 494-516, 1981.
- McElroy, M.B., T.Y. Kong Y.L. Yung, Photochemistry and Evolution of Mars' Atmosphere: A Viking Perspective, *J. Geophys. Res.* **82**, 4379-4388, 1977.

- McLaren, A.D. and D. Shugar, Photochemistry of Proteins and Nucleic Acids, Pergamon, Oxford, 1964.
- Margulis, L., P. Mazur, E.S. Barghoorn, H.O. Halvorson, T.H. Jukes, I.R. Kaplan, The Viking Mission: Implications for Life on Mars, *J. Mol. Evol.* **14**, 223-232, 1979.
- Mazur, P., E.S. Barghoorn, H.O. Halvorson, T.H. Jukes, I.R. Kaplan and L. Margulis, Biological Implications of the Viking Mission to Mars, *Space Sci. Rev.* **22**, 3-34, 1978.
- Mills, A.A., Dust Clouds and Frictional Generation of Glow Discharges on Mars, *Nature* **268**, 614, 1977.
- Nussinov, M.D., Y.B. Chernyak, and J.L. Ettinger, Model of the Fine-Grain Component of Martian Soil Based on Viking Lander Data, *Nature* **274**, 859-861, 1978.
- Oró, J. and Holzer, G., The Photolytic Degradation and Oxidation of Organic Compounds Under Simulated Martian Conditions, *J. Mol. Evol.* **14**, 153-160, 1979.
- Oyama, V.I., The Gas Exchange Experiment for Life Detection: The Viking Mars Lander, *Icarus* **16**, 167-184, 1972.
- Oyama, V.I., B.J. Berdahl, G.C. Carle, M.E. Lehwalt and H.S. Ginoza, The Search for Life on Mars: Viking 1976 Gas Changes as Indicator of Biological Activity, *Origins of Life* **7**, 313-333, 1976.

- Oyama, V.I. and B.J. Berdahl, The Viking Gas Exchange Experiment Results from Chryse and Utopia Surface Samples. *J. Geophys. Res.* **82**, 4669-4676, 1977.
- Oyama, V.I., B.J. Berdahl, and G.C. Carle, Preliminary Findings of the Viking Gas Exchange Experiments and a Model for Martian Surface Chemistry, *Nature* **265**, 110-114, 1977.
- Oyama, V.I., B.J. Berdahl, F. Woeller, and M. Lehwalt, The Chemical Activities of the Viking Biology Experiments and the Arguments for the Presence of Superoxides, Peroxides, $\gamma\text{Fe}_2\text{O}_3$ and Carbon Suboxide Polymer in the Martian Soil, *Life Sci. Space. Res.* **16**, 3-8, 1978.
- Oyama, V.I. and B.J. Berdahl, A Model of Martian Surface Chemistry, *J. Mol. Evol.* **14**, 199-210, 1979.
- Pang, K.D., S.F. Chun, J. M. Ajello, Z. Nansheng, and L. Minji, Organic and Inorganic Interpretations of the Martian UV-IR Reflectance Spectrum, *Nature* **295**, 43-46, 1982.
- Parkinson, T.M. and D.M. Hunten, Spectroscopy and Aeronomy of O_2 on Mars, *J. Atmos. Sci.* **29**, 1380-1390, 1972.
- Plumb, R.C., R. Tantayanon, M. Libby, and W.W. Xu, Chemical Model for Viking Biology Experiments: Implications for the Composition of the Martian Regolith, *Nature* **338**, 633-635, 1989.
- Ponnamperuma, C., A. Shimoyama, M. Yamada, T. Hobo, and R. Pal, Possible

- Surface Reactions on Mars: Implications for Viking Biology Results, *Science* **197**, 455-457, 1977.
- Pollack, J.B., T. Roush, F. Witteborn, J. Bregman, D. Wooden, C. Stoker and O.B. Toon, Thermal Emission Spectra of Mars (5.4-10.5 μm): Evidence for Sulfates, Carbonates, and Hydrates, *J. Geophys. Res.* in press, 1989.
- Pollack, J.B., J.F. Kastings, S.M. Richardson and K. Poliakoff, The Case for a Wet, Warm Climate on Early Mars, *Icarus* **71**, 203-224, 1987.
- Sancier, K.M. and H. Wise, Photoassisted Oxidation of Organic Material Catalyzed by Sand, *Atm. Environ.* **15**, 639-640, 1981.
- Scatterfield, C.N. *Mass Transfer in Heterogenous Catalysis*, MIT Press, Cambridge, Mass, 1970.
- Schumb, W.C., C.N. Scatterfield and R.L. Wentworth, *Hydrogen Peroxide*, Reinhold, New York, 1955.
- Shimazaki, T., Photochemical Stability of CO_2 in the Martian Atmosphere: Reevaluation of the Eddy Diffusion Coefficient and the Role of Water Vapor, *J. Geomag. Geoelectr.* **41**, 273-301, 1989.
- Singer, R.B. Spectral Evidence for the Mineralogy of High Albedo Soils and Dust on Mars, *J. Geophys. Res.* **87**, 10159-10168, 1982.
- Smoluchowski, R., Mars: Retention Of Ice, *Science* **159**, 1348-1350, 1968.
- Wright, I.P., M.M. Grady and C.T. Pillinger, Organic Materials in a Martian Meteorite, *Nature* **340**, 220-222, 1989.

Zill, L.P., R. Mack and D.L. DeVincenzi, Mars Ultraviolet Simulation Facility,
J. Mol. Evol. **14**, 79-89, 1979.

Zent, A. P., F. P. Fanale, J. R. Salvail, S. E. Postawko, Distribution and State
of H₂O in the High-Latitude Shallow Subsurface of Mars, *Icarus* **67**, 19 -
38, 1986.