

# **Investigation of the Atmosphere-Snow Transfer Process for Hydrogen Peroxide**

by

Joseph Robert McConnell

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A Dissertation Submitted to the Faculty of the  
DEPARTMENT OF HYDROLOGY AND WATER RESOURCES

In Partial Fulfillment of the Requirements

For the Degree of

DOCTOR OF PHILOSOPHY  
WITH A MAJOR IN HYDROLOGY

In the Graduate College

THE UNIVERSITY OF ARIZONA

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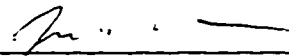
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## ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation's Office of Polar Programs (OPP-9123025 and OPP-9224192) and a National Aeronautics and Space Administration's Mission to Planet Earth Graduate Fellowship for Global Change (NGT 30269). Work at South Pole was made possible by a cooperative agreement with the NOAA Climate Monitoring and Diagnostics Laboratory. Atmospheric photochemical modeling at NASA was supported by the Goddard Director's Discretionary Fund. To all of these agencies, many thanks. The assistance of the staff of Antarctic Support Associates at South Pole (1994-95, 1995-96) and of the Polar Ice Coring Office, both in Lincoln and Greenland (1994, 1995), was much appreciated. Special thanks to K. McNitt and R. Ramos of the NOAA Climate Monitoring and Diagnostics Laboratory for their heroic efforts collecting snow samples year-round at South Pole. R. Brice has been a constant help with computer-related issues and B. Snider and J. Winterle a great help in the lab and in the field. Finally, special thanks to my advisor, R. Bales, for his support and efforts. The intellectual independence that he allowed me in pursuing this research was much appreciated.

## DEDICATION

This is dedicated to my parents, William and Virginia McConnell, for endowing me with a life long interest in learning and to my wife, Patricia, and children, Kate and Jamie, without whose love, support, encouragement, and indulgence, this would not have been possible.

## TABLE OF CONTENTS

<b>LIST OF FIGURES . . . . .</b>	<b>9</b>
<b>LIST OF TABLES . . . . .</b>	<b>13</b>
<b>ABSTRACT . . . . .</b>	<b>14</b>
<b>1. Introduction . . . . .</b>	<b>16</b>
1.1. Scope of Research . . . . .	16
1.2. Pertinence of Research . . . . .	17
<b>2. Summary of Important Findings . . . . .</b>	<b>21</b>
2.1. Summary of Paper #1: A lumped parameter model for the atmosphere-to-snow transfer function for hydrogen peroxide . . . . .	21
2.2. Summary of Paper #2: Physically based modeling of atmosphere-to-snow-to-firn transfer of $H_2O_2$ at South Pole . . . . .	23
2.3. Summary of Paper #3 Physically based inversion of surface snow concentrations of $H_2O_2$ to atmospheric concentrations at South Pole . . . . .	26
2.4. Summary of Paper #4: Recent Intra-Annual Snow Accumulation at South Pole: Implications for Ice Core Interpretation . . . . .	28
<b>3. Implications of Important Findings . . . . .</b>	<b>31</b>
3.1. Synthesis of Papers: . . . . .	31
3.2. Implications of Findings: . . . . .	35
<b>Appendix A. A Lumped Parameter Model for the Atmosphere-to-Snow Transfer Function for Hydrogen Peroxide . . . . .</b>	<b>43</b>
A.1. Introduction . . . . .	45
A.2. Model . . . . .	46
A.2.1. Five-Parameter Transfer Function Model . . . . .	46
A.2.2. Vapor-Diffusion Model . . . . .	47
A.3. Methods . . . . .	47
A.4. Results . . . . .	48
A.4.1. Field Measurements . . . . .	48

A.4.2. Model Fits . . . . .	49
A.5. Discussion . . . . .	50
A.6. Conclusions . . . . .	51

<b>Appendix B. Physically Based Modeling of Atmosphere-to-Snow-to-Firn Transfer of H<sub>2</sub>O<sub>2</sub> at South Pole . . . . .</b>	<b>53</b>
B.1. Introduction . . . . .	56
B.2. Methods . . . . .	58
B.2.1. Year Round Surface Snow Samples . . . . .	58
B.2.2. Snow Pits at Accumulation Stakes . . . . .	58
B.2.3. Short Term Atmospheric H <sub>2</sub> O <sub>2</sub> Measurements . . . . .	59
B.3. Models . . . . .	59
B.3.1. Atmospheric Photochemical Modeling . . . . .	59
B.3.2. Snow Pack Ventilation Modeling . . . . .	60
B.3.3. Snow Pack Temperature Modeling . . . . .	62
B.3.4. Chemical Transfer and Snow Pack Model . . . . .	62
B.3.5. Snow Pack Model Summary . . . . .	64
B.4. Results . . . . .	66
B.4.1. Surface Snow Simulations . . . . .	66
B.4.2. Snow Pit Simulations . . . . .	67
B.5. Discussion . . . . .	68
B.5.1. Surface Snow Simulations . . . . .	68
B.5.2. Snow Pit Simulations . . . . .	69
B.6. Conclusions . . . . .	71

<b>Appendix C. Physically Based Inversion of Surface Snow Concentrations of H<sub>2</sub>O<sub>2</sub> to Atmospheric Concentrations at South Pole . . . . .</b>	<b>88</b>
C.1. Introduction . . . . .	91
C.2. Methods . . . . .	91
C.3. Model . . . . .	92
C.4. Results . . . . .	93
C.4.1. Atmospheric Photochemical Model Estimates . . . . .	93
C.4.2. Inversion Model Results . . . . .	93
C.5. Discussion . . . . .	93
C.6. Conclusions . . . . .	94

<b>Appendix D. Recent intra-annual snow accumulation at South Pole: Implications for ice core interpretation . . . . .</b>	<b>95</b>
D.1. Introduction . . . . .	98
D.2. Methods . . . . .	99

D.2.1. Data . . . . .	99
D.2.2. Fitting Gamma Distributions to Preserved Monthly Accumulation . . . . .	99
D.3. Results . . . . .	100
D.4. Discussion . . . . .	101
D.4.1. Independence of Monthly Accumulation . . . . .	101
D.4.2. Interannual Accumulation . . . . .	102
D.4.3. Extension to Other Polar Ice Coring Sites . . . . .	103
D.5. Conclusions . . . . .	104
<b>REFERENCES . . . . .</b>	<b>106</b>



## LIST OF FIGURES

3.1. Processes and steps involved in the transfer function relating concentrations in ice to those in the atmosphere. . . . .	40
3.2. Observed snow pit (solid), firn core (dot-dash) and physically based model simulations (dot) of $\text{H}_2\text{O}_2$ concentrations in snow and firn at (a) South Pole and (b) Siple Dome, Antarctica. In the simulations, annual accumulation was replicated from year to year and distributed uniformly throughout the year so individual summer peaks and winter troughs in the model results will not coincide with observations. Trends in observed and simulated concentration changes with depth are well matched at both sites, indicating that the physically based transfer model has wide applicability. .	41
3.3. Preliminary firn core concentrations of $\text{H}_2\text{O}_2$ at South Pole plotted against (a) depth and (b) time. Note the strong decrease in concentration to about 5 m, followed by a slower decline to ~ 13 m. The time of rapid change coincides with the development of the stratospheric ozone hole over Antarctica that began in the early 1970s. . . . .	42
A.1. The atmosphere-snow log concentration ratios for $\text{H}_2\text{O}_2$ from the three pits as a function of temperature at the time of accumulation. The "ADG effective equilibrium" is a best fit to these data. The laboratory equilibrium line is a fit to measurements reported by <i>Conklin et al.</i> [1993]; the codeposition and Henry's Law ( $K_H$ ) lines are calculated. . . . .	46
A.2. $\text{H}_2\text{O}_2$ concentrations, $\delta^{18}\text{O}$ , and timing of accumulation from the three snow pits dug beneath ADG's at Summit, Greenland: a) Kenton AWS, b) GISP2 AWS, and c) GISP2 thermocouple pits. The dashed lines represent extrapolated accumulation histories. . . .	48
A.3. Snow $\text{H}_2\text{O}_2$ concentrations, air temperature, measured and modeled atmospheric $\text{H}_2\text{O}_2$ concentrations, and $\delta^{18}\text{O}$ plotted against time. Note that in order to illustrate changes over a calendar year, the field data have been split with June to December, 1994 plotted on the upper half and January to June, 1995 plotted on the lower half of the graph. . . . .	48

A.4. Measured air temperature (dashed) and the accumulation temperature implied by the measured $\delta^{18}\text{O}$ values in the snow pits (symbols) plotted against season of year. $\delta^{18}\text{O}$ temperature ( $^{\circ}\text{C}$ ) is calculated using the following relation given by <i>Cuffey et al.</i> [1992]: $T = \frac{\delta^{18}\text{O} + 18.2}{0.53}$ , where $\delta^{18}\text{O}$ is in per mil. . . . .	49
A.5. Selected orthogonal objective function surfaces from the five-parameter transfer function model optimization using the thermocouple-string pit data. . . . .	49
A.6. Log concentration ratios for $\text{H}_2\text{O}_2$ as a function of temperature resulting from parameter estimation using the automatic-depth-gage snow-pit data. For all three cases, the surface interaction ( $z_{\text{efold}}$ ) and disequilibrium terms ( $S_{\text{eq}}$ ) were $0.72 \text{ m y}^{-1}$ and $1.05 \text{ y m}^{-1}$ respectively. Laboratory equilibrium, codeposition, and ADG effective equilibrium lines are from Figure 1. . . . .	50
A.7. Modeled $\text{H}_2\text{O}_2$ profiles with depth for the three ADG pits: (a) Kenton AWS, (b) GISP2 AWS, (c) GISP2 thermocouple pit. . . . .	50
A.8. Example synthetic snow pit $\text{H}_2\text{O}_2$ profiles with various accumulation histories: a) uniform at $60 \text{ cm y}^{-1}$ , b) uniform at $30 \text{ cm y}^{-1}$ , c) uniform at $120 \text{ cm y}^{-1}$ , and d) sporadic around $60 \text{ cm y}^{-1}$ . The dashed line is the pit average concentration. . . . .	50
B.1. Map of the long term, snow stake accumulation field with locations of snow pits indicated. . . . .	78
B.2. Time-depth map for the four snow pits sampled at South Pole in January, 1996 . . . . .	78
B.3. Spot measurement (circles) of atmospheric $\text{H}_2\text{O}_2$ at South Pole and the repeated annual cycle used in surface snow and snow pack simulations. The latter was estimated using a 1-D photochemical box model [ <i>McConnell et al.</i> , 1997c]. . . . .	79
B.4. Modeled snow pack ventilation at South Pole. High wind conditions (dotted) assumed a surface forcing pressure of 2.5 Pa and low wind 0.25 Pa (dash-dot). Winter and spring (filled circles) snow packs included a high density, fine-grained wind pack layer at the surface. Summer (diamonds) snow packs did not include this layer. The ventilation rate with depth used in snow pack simulations is indicated (solid). . . . .	80
B.5. SNTHERM model snow pack temperatures used in the snow pack simulations at 0.01, 0.10, 0.5, 1.0, 2.0 (heavy line) . and 4.0 m. .	81

B.6. Snow-atmosphere partitioning relations determined by laboratory experiments [Conklin <i>et al.</i> , 1993] and previous transfer modeling at South Pole [McConnell <i>et al.</i> , 1997c]. Co-deposition refers to equal rate of condensation of $H_2O$ and $H_2O_2$ , resulting in the same molar ratio in frozen particles as in the air. . . . .	81
B.7. $H_2O_2$ concentrations (a) and sample depth (b) in surface snow at South Pole. Error bars show 1 standard deviation. . . . .	82
B.8. Observed (circles) and simulated surface snow concentrations at South Pole for effective snow grain radii of 80 (dashed), 40 (dotted) and 20 (solid) $\mu m$ . . . . .	83
B.9. Measured (solid) and simulated (dashed) concentration profiles for 4 snow pits at South Pole. The pits were sampled in January, 1996. . . . .	83
B.10. Measured (solid) and simulated (dashed) formation temperature profiles for the snow pits in Figure 12. . . . .	84
B.11. Snow pack simulation (a) using mean monthly accumulation at South Pole (following McConnell <i>et al.</i> , [1997b]). For comparison with observations, the running annual average for the pit simulation (a) is plotted with the observed profiles at stakes 01 (b), 06 (c), 10 (d), and 31 (e). Note that the simulation curve is generally lower than the observed profiles, indicating that the snow pack model may be under predicting the snow concentration with depth. . . . .	85
B.12. Distribution of $H_2O_2$ in snow grains during simulations of surface snow concentrations. Response of the inner shell (dashed) lags the mean (solid) by approximately 5 weeks for an 80 $\mu m$ grain radius while that of the outer shell (dotted) leads. . . . .	86
B.13. The dependence of annual average $H_2O_2$ in simulated snow pits approximately 10 years after burial on annual accumulation rate. Current South Pole annual accumulation was modeled as 0.29 m. . . . .	87
C.1. Snow-atmosphere partitioning relations determined by laboratory experiments [Conklin <i>et al.</i> , 1993] and this study. Co-deposition refers to equal rate of condensation of $H_2O$ and $H_2O_2$ , resulting in the same molar ratio in frozen particles as in the air. . . . .	92
C.2. Simulated response of $H_2O_2$ concentration in spherical ice grains (200 $\mu m$ radius) to changes in temperature from a) -40 °C to -30 °C and b) -40 °C to -20 °C. Simulated temperatures increase at 4 weeks and return to -40 °C at 20 weeks. Gas-phase $H_2O_2$ is 100 pptv. . . . .	92
C.3. Histogram (a) and associated cumulative distribution function (b) of recent monthly snow accumulation at South Pole based on 50 stakes measured over a 7.5 year period [McConnell <i>et al.</i> , 1996a]. . . . .	93

C.4. Measured concentrations of $\text{H}_2\text{O}_2$ in surface snow (a) and computed surface snow temperature (b) at South Pole. Temperature estimates computed using an energy balance model [Liston, 1995] from measurements routinely collected by NOAA of air temperature, wind speed, and relative humidity. . . . .	93
C.5. Atmospheric concentrations of $\text{H}_2\text{O}_2$ at South Pole: (a) estimated from a photochemical box model using multi-year-averaged seasonal cycles in measured $\text{O}_3$ , CO, temperature, relative humidity, and ozone burden; error bars represent expected variability from short term changes in these values; and (b) box model estimates extrapolated to the full annual cycle and using measured relative humidity, compared with the optimized inversion of the surface snow samples and atmospheric measurements. . . . .	93
D.1. Hydrogen peroxide in surface snow at South Pole. Error bars represent 1 standard deviation. . . . .	99
D.2. Map of the the snow stake accumulation field, which is located just outside of the clean air sector, about 400 m grid east of Amundsen-Scott Station, Antarctica. . . . .	99
D.3. Time-depth map for an individual accumulation stake showing both gross monthly accumulation and net preserved accumulation. . .	100
D.4. Distribution of the sample mean as the number of samples increases from 1 to 30. The shape $\alpha$ and scaling $\lambda$ parameters for the November gamma distribution were used for illustration (Table 1).100	100
D.5. Histograms of gross and net preserved monthly accumulation for all 50 stakes and all measurement periods. . . . .	101
D.6. Monthly histograms of net preserved accumulation data for all 50 stakes. Solid lines are fitted gamma distributions. . . . .	101
D.7. Standard deviation of gross monthly accumulation over the 50 accumulation stakes and corresponding monthly maximum winds. . .	103
D.8. Standard deviation of gross monthly accumulation over 50 accumulation stakes (June 1991 through December 1995) plotted against a proxy record of snow transport by wind during each accumulation month. . . . .	104

## LIST OF TABLES

D.1. Monthly Accumulation Statistics and Fitted Gamma Distribution Parameters for South Pole and Computed Averaging Times for Three Proportional Error Limits $\epsilon$ . . . . .	102
D.2. Seasonal Accumulation Statistics and Fitted Gamma Distribution Parameters for South Pole and Computed Averaging Times for Three Proportional Error Limits $\epsilon$ . . . . .	102
D.3. Estimated Monthly Accumulation Statistics for Summit, Greenland, and Computed Averaging Times for Three Proportional Error Limits $\epsilon$ . . . . .	104

## ABSTRACT

Of the three primary atmospheric oxidants, hydroxyl radical, ozone, and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), only the latter is preserved in ice cores. To make quantitative use of the ice core archive, however, requires a detailed understanding of the physical processes that relate atmospheric concentrations to those in the snow, firn and thence ice. The transfer processes for  $\text{H}_2\text{O}_2$  were investigated using field, laboratory, and computer modeling studies. Empirically and physically based numerical algorithms were developed to simulate the atmosphere-to-snow-to-firn transfer processes and these models coupled to a snow pack accumulation model. The models, tested using field data from Summit, Greenland and South Pole, indicate that  $\text{H}_2\text{O}_2$  is reversibly deposited to the snow surface, with subsequent uptake and release controlled by advection of air containing  $\text{H}_2\text{O}_2$  through the top meters of the snow pack and temperature-driven diffusion within individual snow grains. This physically based model was successfully used to invert year-round surface snow concentrations to an estimate of atmospheric  $\text{H}_2\text{O}_2$  at South Pole. Field data and model results clarify the importance of accumulation timing and seasonality in determining the  $\text{H}_2\text{O}_2$  record preserved in the snow pack. A statistical analysis of recent accumulation patterns at

South Pole indicates that spatial variability in accumulation has a strong influence on chemical concentrations preserved in the snow pack.

## CHAPTER 1

### Introduction

#### 1.1 Scope of Research

In order to quantitatively interpret ice-core records of  $\text{H}_2\text{O}_2$  and other chemical species as proxies for atmospheric concentrations, a physically based understanding of the transfer processes from atmosphere-to-snow-to-firn-to-ice is required.  $\text{H}_2\text{O}_2$  was chosen as the focus of this study both because of its importance in understanding oxidation capacity of the atmosphere but also because it is seen as representative of reversibly deposited species in general. This dissertation consists of four papers that are associated with atmosphere-snow chemical transfer processes for  $\text{H}_2\text{O}_2$ . Two papers address forward chemical transfer modeling where 1) an empirical model and 2) a physically based model were designed and used to simulate snow pit data at Summit, Greenland and South Pole respectively. A third paper used a physically based model to invert surface snow concentrations of  $\text{H}_2\text{O}_2$  at South Pole to an estimate of the annual atmospheric concentration cycle. The final paper used year-round, monthly accumulation data from South Pole to describe statistically how snow accumulates there.



## 1.2 Pertinence of Research

The oxidizing capacity of the atmosphere is a function of the atmospheric concentrations of ozone, hydroxyl radical, and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). It is important in understanding past and future global climate change because the oxidation capacity determines the atmospheric lifetimes of most trace gases. Models for investigating changes in atmospheric oxidation capacity require historical data for validation [Thompson, 1992]. While polar ice cores provide a detailed record of past changes in atmospheric chemistry and meteorology [Wolff, 1996], of the primary oxidants, only  $\text{H}_2\text{O}_2$  is archived. To make use of the archive in the ice, however, requires a detailed understanding of the transfer processes or functions that relate atmospheric concentrations to those in the snow and firn and thence ice.

Most aerosols are irreversibly deposited to snow. That is, once deposited to the surface through either wet or dry deposition, they are not emitted back to the atmosphere. Even for these non-volatile species, transfer processes are often highly non-linear since deposition efficiencies can depend on such factors as precipitation formation [Bergin *et al.*, 1995], accumulation seasonality [Davidson *et al.*, 1996] and snow pack ventilation whereby concentrations can be enhanced or reduced by advecting air [Harder *et al.*, 1996; Cunningham and Waddington, 1993; Waddington *et al.*, 1996].

Unlike aerosols, volatile species such as  $\text{H}_2\text{O}_2$ , formaldehyde, and organic acids are reversibly incorporated in the snow because a fraction of the deposited mass of

these species cycles between the atmosphere and snow as precipitation ages and as surface and near-surface conditions change [*Legrand et al.*, 1996; *Bales et al.*, 1992; *Bales and Wolff*, 1995].

Models of chemical transfer are most readily formulated in the forward direction, i.e., atmosphere-to-snow-to-firn-to-ice, and can help lead to an understanding of the underlying physical processes [*Waddington*, 1996]. *Bergin et al.* [1996] developed a model for atmosphere-to-snow transfer through fog deposition and compared simulations with surface samples at Summit, Greenland. In the first of two forward modeling papers included in this dissertation, "A lumped parameter model for the atmosphere-to-snow transfer function for hydrogen peroxide" [*McConnell et al.*, 1997b] (Appendix A), we developed an empirical model to simulate atmosphere-to-snow transfer and then used the model to simulate snow pit concentration profiles at Summit. In the second forward modeling paper, "Physically based modeling of atmosphere-to-snow-to-firn transfer of  $\text{H}_2\text{O}_2$  at South Pole" (Appendix B), we developed a physically based model and used this to simulate both year-round surface snow concentrations and snow pit concentration profiles at South Pole. In the snow pit applications of both models, a priori information on accumulation history was used. Long term model simulations using synthetic accumulation records were used to investigate the preservation of  $\text{H}_2\text{O}_2$  at depth and the impact of annual accumulation rate on preserved  $\text{H}_2\text{O}_2$ .

The quantitative interpretation of an ice core record requires inverse, rather than forward modeling, i.e., ice-to-firn-to-snow-to-atmosphere. Inverse models have been used to estimate atmospheric concentrations for non-reactive gases such as methane and halocarbons using measurements of firn air for recent atmospheres [*Battle et al.*, 1996] and air bubbles trapped in ice for older atmospheres extending back as much as 160,000 years [*Barnola et al.*, 1995; *Chappelaz et al.*, 1990; *Schwander*, 1996]. In the third paper of this dissertation, "Physically based inversion of surface snow concentrations of  $\text{H}_2\text{O}_2$  to atmospheric concentrations at South Pole" [*McConnell et al.*, 1997c] (Appendix C), we developed a physical model for diffusion in snow grains and then, assuming that uptake and release of  $\text{H}_2\text{O}_2$  are driven by temperature and atmospheric concentration, inverted year-round surface snow samples to an estimate of the annual cycle in atmospheric  $\text{H}_2\text{O}_2$ .

Estimation of past atmospheric conditions and chemistry by interpretation of ice core concentrations necessarily requires transformation from depth to time. Depth-time curves are typically based on layer counting where peaks or troughs in seasonally varying chemical species, dust, electrical conductivity, and stable oxygen isotopes are used as time markers [*Jouzel et al.*, 1983]. Known volcanic markers and bomb fallout are used as long term controls in the layer counting [*Zielinski et al.*, 1994]. For lack of better resolution, intra-annual accumulation is usually assumed to be linear between these annual markers but non-linearities in the intra-annual time-depth relationship, as well as missing or indistinct annual peaks, greatly restrict the

quantitative interpretation of ice core chemical profiles, particularly for seasonally varying species [Steig *et al.*, 1994]. Most chemical species of interest, including  $\text{H}_2\text{O}_2$ , show strong seasonal variations [Beer *et al.*, 1991; Fischer and Wagenbach, 1996].

Much of the temporal variability in snow accumulation that distorts the time-depth relations comes from spatial variability in accumulation. This has been attributed to redistribution of new snow by wind. Fisher *et al.* [1985] used ice cores from Greenland and the Canadian Arctic to investigate core-to-core variability and concluded that, especially for chemical species that diffuse in the snow pack, many decades of averaging are required to sufficiently reduce the “noise” caused by this spatial variability. In the fourth paper included in this dissertation, “Recent inter-annual snow accumulation at South Pole: implications for ice core interpretation” [McConnell *et al.*, 1997a] (Appendix D), we used recent, year-round monthly accumulation data from South Pole to first model monthly snow accumulation statistically and then to investigate the implications of these statistics on ice core interpretation.

## CHAPTER 2

### Summary of Important Findings

The methods, results, and conclusions of my research are presented in papers appended to this dissertation. The following is a summary of the most important findings presented in the four papers.

#### **2.1 Summary of Paper #1: A lumped parameter model for the atmosphere-to-snow transfer function for hydrogen peroxide**

This was the first paper in the literature where an attempt was made to quantitatively synthesize field observations of atmospheric concentration, snow pit concentration profile, and snow accumulation data with laboratory results in a chemical transfer model. The model, while empirical, included an atmosphere-to-snow transfer component coupled to a snow pack simulation model. Three terms were used to define the logarithm of the thermodynamic equilibrium partitioning relationship between air and snow. A fourth parameter reflected the disequilibrium that may be preserved because of rapid burial. A fifth term described the interaction of surface

atmospheric conditions with already buried snow. The model was parameterized using objective comparison of simulations with three snow pit profiles, each spanning 1 year of accumulation at Summit, Greenland where an independent record of snow accumulation for each pit was available from automatic snow depth gauges. The major findings of this study follow.

**(1) Interaction of the surface air diminishes very rapidly with depth.** Optimized model results indicated penetration depths of only about 0.024 m into the snow pack in 0.033 years. While consistent with “retarded” diffusion concepts, this penetration depth is far less than for more familiar, less reactive species such as methane or carbon dioxide.

**(2) Periods of rapid accumulation allow snow to be buried while still well out of thermodynamic equilibrium.** That is, the model confirmed previous qualitative observations that summer layers in particular are preserved well out of equilibrium while winter layers are preserved closer to equilibrium. Analysis of the model optimization showed that, in agreement with grain diffusion modeling based on laboratory data, snow formed at co-deposition will on average release about 85% of its excess  $\text{H}_2\text{O}_2$  back to the atmosphere before burial.

(3) Accumulation seasonality plays a key role in determining the levels of  $\text{H}_2\text{O}_2$  preserved in the firn record. When analyzed using the snow pack accumulation model, the large variability in  $\text{H}_2\text{O}_2$  measured in the three snow pits, each spanning the same year and located no more than 30 km apart, demonstrated that accumulation timing is a dominant factor in determining preserved  $\text{H}_2\text{O}_2$  levels.

(4) Because of this strong dependence on seasonality, atmosphere-to-snow transfer modeling must include an independent estimate of accumulation timing.

(5) The final preserved  $\text{H}_2\text{O}_2$  level is, to a significant degree, determined by the annual accumulation rate. While empirical and tested on snow pits spanning a single year, the model indicated that both the amplitude and mean of the preserved  $\text{H}_2\text{O}_2$  depends on annual accumulation rate.

## 2.2 Summary of Paper #2: Physically based modeling of atmosphere-to-snow-to-firn transfer of $\text{H}_2\text{O}_2$ at South Pole

A physically based chemical transfer and snow pack model, based on the advection-dispersion equation and spherical diffusion within representative snow grains, was developed and tested using field data from South Pole. This study built on our previous

transfer work at South Pole (Appendix C) by extending the physically based model down into the snow pack. The field data included a unique, 2-year set of weekly surface snow samples collected year-round at South Pole, short-term atmospheric measurements, and 4 snow pits. These were located at stakes in a long-term snow accumulation stake array so a year-round, monthly record of snow accumulation was available for the entire time spanned by the pits. Unlike the earlier snow pack model used in Greenland, these snow pack simulations included no parameter fitting and all snow pack characteristics like ventilation and temperature were estimated independently using established physical models. In addition, each pit spanned between 4 and 5 years, much longer than the 1 year pits at Summit. The most significant findings are listed below.

(1) **More than 2-years of year-round surface snow sampling and associated modeling demonstrates that there is a pronounced, repeatable cycle of  $\text{H}_2\text{O}_2$  in near-surface snow at South Pole, driven primarily by temperature.** The very pronounced peak in surface snow concentration occurs in mid-November, well before the summer solstice, showing that the “summer” peak in  $\text{H}_2\text{O}_2$  at South Pole, and possibly many other polar sites, is actually a spring peak. This has important implications for water equivalent accumulation studies that use annual peaks/troughs in ice cores as time markers. Photochemical modeling indicates that the peak atmospheric concentration occurs much closer to the solstice, so that it



is the temperature dependence in snow/atmosphere partitioning relation that shifts the peak in snow concentration well into the spring.

(2) Atmosphere-to-snow-firn transfer of  $\text{H}_2\text{O}_2$  at South Pole can be modeled by advection of surface air through the top few meters of the pack and diffusion of  $\text{H}_2\text{O}_2$  into and out of snow grains in response to changing atmospheric concentrations and snow pack temperatures. The physically based snow pack model successfully captured much of the variability in the observed snow pit concentration profiles with depth using the available monthly accumulation histories. Simulations of formation temperature (air temperature at the time of layer accumulation) are in good agreement with formation temperature calculated directly from measured  $\delta^{18}\text{O}$  profiles, indicating that the snow accumulation histories are approximately correct.

(3) Accumulation seasonality is a dominant factor in determining the levels of  $\text{H}_2\text{O}_2$  and  $\delta^{18}\text{O}$  preserved in the firn record. As with the empirical snow pack modeling at Summit, the very large variability in observed snow pit concentration profiles covering the same time spans and located no farther than 50 meters apart, as well as model simulations using the monthly accumulation data, indicated that intra-annual accumulation timing is very important in determining  $\text{H}_2\text{O}_2$  and  $\delta^{18}\text{O}$  levels in the snow pack.

(4) Long-term snow pack simulations indicate that firn continues to lose  $\text{H}_2\text{O}_2$  to the atmosphere for at least 10-12 years ( $\sim 3$  m) after burial at current South Pole temperatures and accumulation rates. Shallow ice core  $\text{H}_2\text{O}_2$  data are required to verify this result but it is far deeper than anticipated.

(5) Long-term model simulations show that preserved  $\text{H}_2\text{O}_2$  levels are sensitive to the magnitude of annual accumulation. This result emphasizes the importance of using physically based models to interpret ice core data since reported variations in ice core  $\text{H}_2\text{O}_2$  may be simply the result of changes in annual accumulation or other accumulation characteristics.

### 2.3 Summary of Paper #3 Physically based inversion of surface snow concentrations of $\text{H}_2\text{O}_2$ to atmospheric concentrations at South Pole

The quantitative interpretation of an ice core chemical record requires inverse modeling, e.g., ice-to-firn-to-snow-to-atmosphere. This study was the first attempt to quantitatively invert snow concentrations to an estimate of the atmospheric concentration through time for any chemical species other than the non-reactive gases such as methane, carbon dioxide, and halocarbons. We developed a physically based model of snow grain diffusion and used a unique set of year-round, weekly surface

snow samples from South Pole from November, 1994 through January, 1996 to estimate the atmospheric concentration. By using only the surface snow record and making the assumption that surface snow is comprised entirely of "old" snow, we avoided both the non-linearities in the time-depth relationship and those processes active beneath the surface. The most important findings of this study are as follows.

(1) **The surface snow acts as an excellent proxy for atmospheric concentrations.** Because the inverted atmospheric concentration compares favorably with both short-term measurements made in November/December, 1994 and January, 1996 and with photochemical model predictions of atmospheric  $\text{H}_2\text{O}_2$ , we concluded that the surface snow acts as an excellent proxy for the atmospheric concentration through time.

(2) **Temperature is the dominant factor determining atmosphere-to-snow transfer at South Pole.** The very pronounced peak in surface snow concentration occurs in mid-November, well before the summer solstice. Photochemical modeling predicts an atmospheric peak much closer to the solstice. Inversion of surface snow samples, using a physically based model with temperature as the driving mechanism, results in an atmospheric estimate that matches that predicted by photochemical models.

(3) The response time of the surface snow is controlled primarily by diffusion of  $\text{H}_2\text{O}_2$  into and out of snow grains, with diffusion rates determined by temperature. The physically based inversion model, which uses spherical diffusion to control uptake and release of  $\text{H}_2\text{O}_2$ , gives an inversion result consistent with observations and photochemical modeling. This diffusion-controlled uptake and release is in agreement with laboratory work reported by *Conklin et al.* [1993] and *Winterle* [1996] .

(4) The annual atmospheric cycle of  $\text{H}_2\text{O}_2$  concentration at South Pole has a peak value of  $\sim 280$  pptv approximately around the summer solstice and a minimum in winter of probably less than  $\sim 1$  pptv. Some asymmetry in the annual cycle exists because of the springtime stratospheric ozone hole. This estimate of the annual atmospheric cycle is the combined result of 1) photochemical modeling, 2) short-term atmospheric measurements, and 3) physically based inversion of year-round surface snow concentrations.

## 2.4 Summary of Paper #4: Recent Intra-Annual Snow Accumulation at South Pole: Implications for Ice Core Interpretation

The seasonality of accumulation plays a key role in determining the levels of  $\delta^{18}\text{O}$ ,  $\text{H}_2\text{O}_2$ , and other seasonally varying chemical species that are preserved in firn

and thence ice cores. An ice core record contains not only a history of changes in the atmosphere but also a history of inter- and intra-annual accumulation at the core site. Because intra-annual accumulation is highly variable from year to year and from site to site, interpretations of ice core chemical records for global change studies typically include multi-year averaging to mitigate the unwanted intra-annual accumulation history. However, the length of required multi-year averaging has not been quantified. In this study, I used a unique record of 7.25 years of year-round snow accumulation from South Pole to statistically analyze monthly accumulation and its variability over short spatial scales. The most important findings are summarized below.

**(1) Preserved snow accumulation at a point can be modeled by a gamma distribution.** The monthly data for all 50 accumulation stakes were binned by month and the histogram of preserved accumulation for each month fit with a gamma distribution. The results indicate that accumulation at a point is sporadic, with long periods of little or no accumulation interrupted by short bursts of rapid accumulation. A primary use for these statistical distributions of monthly accumulation is in understanding the significance of short term deviations in observed ice core concentrations. That is, are these deviations indicative of atmospheric changes or simply the result of spatial variability in accumulation. Moreover, these distributions allow the construction of synthetic accumulation records to be used in snow pack model

sensitivity studies (e.g., Monte Carlo simulations) and simulations of ice cores where no record of snow accumulation is available.

(2) At South Pole, multi-year averages of up to 300 years may be required to mitigate the history of monthly accumulation contained in an ice core chemical record. Using the gamma distributions of monthly accumulation, 300 years of averaging are required to have, within the 95% confidence interval, a sample population monthly mean for each month within 20% of the distribution mean. Here, the sample population is defined as those years within the multi-year average.

(3) Multi-year averages of up to 300 years are required for Summit, Greenland. By correlating the spatial variability in monthly accumulation with observed peak wind speeds and accounting for mean monthly accumulation, the statistical results were extrapolated to conditions at Summit, Greenland. While averaging times were expected to be much lower at Summit than at South Pole because of the much larger annual accumulation rate, the month of minimum accumulation at Summit coincides with the month of maximum wind speed, leading to the 300 year requirement. Recently, *Kuhns et al. [in preparation]* have independently estimated similar required averaging times for the central Greenland plateau.

## CHAPTER 3

### Implications of Important Findings

Results and conclusions are presented in each of the individual papers appended to this dissertation. In the following, the important findings of the individual papers are synthesized and the implications of the combined findings discussed.

#### 3.1 Synthesis of Papers:

During the course of this research, modeling of the forward atmosphere-to-snow-to-firn transfer process has progressed from empirically based (Appendix A) to physically based (Appendices B and C). Hence, the results of the empirically based modeling have to some extent been replaced by the physically based model, which incorporates our current understanding of the transfer processes.

Our understanding of the physical transfer processes is summarized in Figure 1.1. The chemical composition and physical characteristics of the local atmosphere, combined with the level of incident UV radiation, determine the concentration of  $\text{H}_2\text{O}_2$  in the local atmosphere. Transport to the surface occurs primarily through

wet deposition, although some additional uptake may occur through dry deposition at or below the snow surface as surface air circulates through the snow pack and as snow pack conditions such as temperature change. Chemical exchange between the atmosphere and snow pack continues while the snow is progressively cut off from contact with the atmosphere during burial. This continues to an unknown maximum depth but probably no deeper than 5 to 10 m under current South Pole conditions. Note that the snow pack is generally over-saturated with respect to  $\text{H}_2\text{O}_2$  since there is usually insufficient time for the snow to release its excess peroxide (partitioning to the snow under co-deposition is an order of magnitude greater than that at equilibrium) before burial.

Transfer efficiency is sensitive to a number of parameters, including temperature, snow pack physical characteristics, ventilation, and accumulation timing. Temperature plays a key role throughout the transfer process since 1) snow-atmosphere partitioning of  $\text{H}_2\text{O}_2$  both at equilibrium and under co-deposition is exponentially related to temperature, 2) snow formation processes depend on temperature and thus scavenging efficiency and snow grain size, and 3) diffusion within the snow grains is exponentially related to temperature and hence the rate of uptake and release of  $\text{H}_2\text{O}_2$  by snow. Snow pack physical parameters (e.g., density, permeability, grain size) are important, both because of the influence on ventilation but also because uptake and release of  $\text{H}_2\text{O}_2$  is strongly dependent on grain radius. Ventilation strongly controls the overall efficiency of atmosphere-to-snow-to-firn transfer, particularly at



and below depths where exchange of  $\text{H}_2\text{O}_2$  by advecting air is the limiting factor. At shallower depths where ventilation is relatively high, the limiting factor is the rate of grain scale diffusion. Accumulation timing plays a role in the transfer efficiency in that high accumulation rates result in more rapid reduction of exchange between snow pack and atmosphere. Moreover, accumulation timing is the primary factor that determines wet deposition. If no precipitation occurs or if none is preserved during some period of time at a snow pit or ice core location, then there will be no record of the atmospheric concentration for that period except that deposited through dry deposition by advected surface air into the snow pack.

In the empirically based modeling (Appendix A), the model parameters determined through objective optimization indicated that the depth of penetration of the surface air concentration was quite small (on the order of 0.025 m e-folding depth for a layer exposed for 2 weeks). Conversely, the physically based modeling results indicated that exchange with the surface continues to greater depth than previously expected ( $> 2\text{m}$ ). Comparing results between models is difficult since the parameters do not have the same meaning and the underlying concepts behind the models are quite different. In addition, the models were applied at different sites (Summit, Greenland and South Pole) with significantly different temperatures and accumulation rates. However, note that in the empirical model the parameter  $M$  described the impact of the current atmospheric concentration on the buried layers at that time. That is, it described the short-term impact on the buried snow layers and not

the cumulative, long-term impact. When compared with short-term penetration of non-reactive gases such as methane or carbon dioxide [Schwander,1996], this penetration depth is quite small and is consistent with retarded diffusion concepts. For long-term, cumulative release of  $\text{H}_2\text{O}_2$ , we have far more confidence in the physical model results. These results indicated that, given an independent estimate of the mean ventilation of the snow pack, release of  $\text{H}_2\text{O}_2$  continues to at least  $\sim 2$  m for current South Pole conditions. The rate of release with depth will vary strongly from site to site because of differences in temperature, accumulation rate, representative grain radius, and the ventilation profile as discussed previously.

As demonstrated by the study of recent accumulation at South Pole (Appendix D), the assumption that a single ice core is representative of regional scale, short-term climate and atmospheric chemistry variability is incorrect for current South Pole conditions and probably for many core sites including Summit, Greenland. Long-term averaging of a single core or shorter term averaging of combined multiple core records is required to overcome spatial and temporal variability in accumulation. The strong dependence of atmosphere-to-snow-to-firm transfer on the rate and timing of accumulation that was indicated by the transfer process modeling (Appendices A, B, and C) emphasizes the need for the collection of multiple cores whenever possible in order to evaluate core-to-core variability even over short distances. Inversion of surface snow samples at South Pole to an estimate of atmospheric concentration (Appendix C) was only possible because of the assumption that timing of accumulation was

relatively unimportant in the very top-most, well-ventilated, small-grained surface snow. Inversion of snow pit and ice core chemical concentrations to a high temporal resolution estimate of atmospheric concentration will require detailed information on snow accumulation at the site.

### 3.2 Implications of Findings:

Physically based modeling of the atmosphere-to-snow-to-firn transfer process for  $\text{H}_2\text{O}_2$  clearly indicates that a record of the local atmospheric concentration is preserved in the surface snow, firn, and ice core; although the record is strongly perturbed by the influence of temperature, snow physical properties, ventilation, and accumulation rate and timing at the core site. For most situations, snow is buried out of thermodynamic equilibrium with the atmosphere. At colder and higher accumulation sites, the snow is preserved more out of equilibrium than at warmer and lower accumulation sites. While this research was focused on  $\text{H}_2\text{O}_2$ , many of the conclusions and the algorithms developed may be applicable to other species showing reversible deposition behavior (e.g.,  $\text{HCHO}$ ,  $\text{HNO}_3$ , organic acids,  $\delta^{18}\text{O}$ ) [Legrand *et al.*, 1996; Neftel, 1996]. While our results indicate that surface adsorption does not play a significant role for  $\text{H}_2\text{O}_2$  at polar temperatures, there is evidence that it may for other species like  $\text{HNO}_3$  [Laird *et al.*, 1996] so additional model development may be necessary.

Figure 1.2 shows preliminary model estimates of  $\text{H}_2\text{O}_2$  concentration and snow pit profiles at two sites in dramatically different depositional environments: South Pole and Siple Dome ( $81^\circ 39' \text{ S}$ ,  $148^\circ 49' \text{ W}$ ). A first firn core concentration measurement at South Pole is also shown. Model parameters for the South Pole simulation were identical to those used in the snow pack simulations reported in Figure 11a, Appendix B. Model parameters for the Siple Dome simulation, derived from the available observations, included an annual air temperature cycle  $26^\circ\text{C}$  warmer than South Pole, a representative snow grain size of  $140 \mu\text{m}$ , and snow pack ventilation identical to that at South Pole. Accumulation timing was replicated from year to year and distributed evenly throughout the year so individual observed summer peaks and winter troughs will not match in the model results.

Comparison of the snow pack simulations and the observed concentration profiles indicates that the physically based model has wide applicability. The model simulates very well both the  $\sim 4$  fold and  $\sim 50$  fold declines in snow pack  $\text{H}_2\text{O}_2$  from the surface to 1 m observed at South Pole and Siple Dome respectively. Simulations of snow pits and ice cores at additional polar sites in Greenland and Antarctica will further validate the transfer model resulting from this research.

For estimating historical levels of  $\text{H}_2\text{O}_2$ , is it better to use cores from warmer, lower accumulation or from colder, higher accumulation sites? When using physically based modeling to actually simulate development of an ice core archive (using *a priori* knowledge or assumptions of accumulation timing, temperature, and ventilation).

these results suggest that colder, higher accumulation sites are preferable since the model will simulate how far out of thermodynamic equilibrium the snow is likely to be preserved. In addition, higher accumulation will result in a higher frequency archive of all chemical species which will aid in estimating and verifying the temperature and accumulation history used in modeling. Conversely, for qualitative interpretation, warmer, lower accumulation sites may be preferred since the preservation level is less sensitive to depositional parameters. That is, preservation is closer to thermodynamic equilibrium. Note, however, that this research unambiguously indicates that simple, qualitative interpretation of an ice core record of  $\text{H}_2\text{O}_2$  from any location as an atmospheric proxy is suspect since transfer efficiency can be so dependent on factors other than atmospheric concentration.

The snow, firn and ice chemical record for  $\text{H}_2\text{O}_2$  contains a record of not only atmospheric  $\text{H}_2\text{O}_2$ , but also of near-surface air temperature, snow pack ventilation and especially accumulation rate and timing. Note that the atmospheric  $\text{H}_2\text{O}_2$  concentration itself is strongly dependent on air temperature and water vapor, in addition to other atmospheric constituents like OH,  $\text{NO}_x$  and  $\text{HO}_2$  concentration and to incident UV radiation. Hence, with sufficient understanding of the underlying physical transfer processes and using *a priori* information on air temperature and ventilation, this chemical record of  $\text{H}_2\text{O}_2$  can be used 1) to estimate the atmospheric concentration of  $\text{H}_2\text{O}_2$  through time or 2) to estimate such phenomena as historical shifts in accumulation timing or seasonality at an ice core site. For the former, independent

information on accumulation rate and timing would be required while for the latter, independent information (e.g., photochemical model results) or assumptions about the atmospheric concentration through time would be necessary. Since ice core concentration profiles of other chemical species contain similar information (e.g.,  $\delta^{18}\text{O}$  for temperature and accumulation timing;  $\text{HNO}_3$  for accumulation timing at some ice core locations), coordinated, simultaneous snow pack modeling of multiple species will result in estimates with the highest levels of confidence.

A preliminary firn core record of  $\text{H}_2\text{O}_2$  at South Pole is shown in Figure 1.3. Note the  $\sim 8$  fold decrease in preserved  $\text{H}_2\text{O}_2$  from 2 to 10 m. The same concentration profile after conversion from depth to time is also shown. Note that the sharp increase in measured snow pack  $\text{H}_2\text{O}_2$  mirrors the development of the stratospheric ozone hole over Antarctica that started in the 1970s. Is this dramatic increase in the firn record indeed a record of stratospheric ozone depletion or is it simply a result of depositional and transfer processes? By using the transfer process model resulting from this research, in combination with the long duration instrumental record of temperature, UV radiation, and atmospheric chemistry available at South Pole and detailed atmospheric photochemical and snow pack ventilation modeling, it will be possible to unravel the depositional and transfer effects from the firn core record to yield a proxy record of atmospheric  $\text{H}_2\text{O}_2$  over the recent past. Because of the well documented, dramatic impact of the springtime stratospheric ozone hole over Antarctica on the local photochemistry at South Pole and the long-term instrumental

record there, a unique opportunity currently exists at South Pole to validate this transfer process model for  $\text{H}_2\text{O}_2$  and to develop and evaluate transfer models for other chemical species using surface snow samples, snow pits, and firn cores.

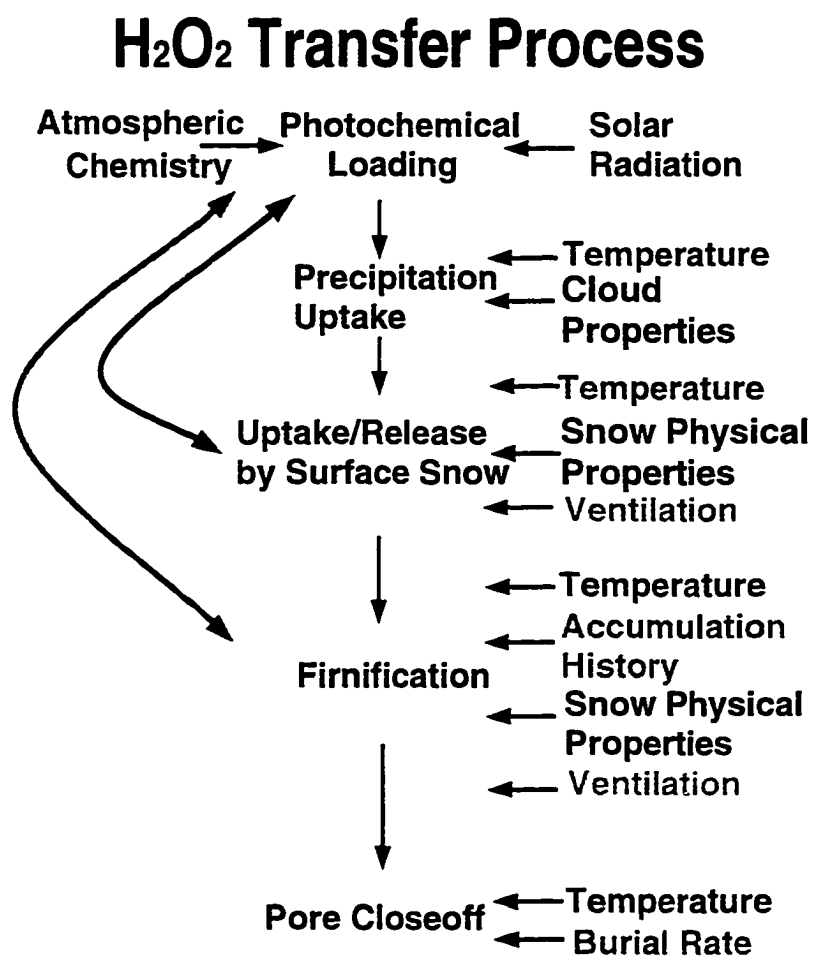


Figure 3.1: Processes and steps involved in the transfer function relating concentrations in ice to those in the atmosphere.



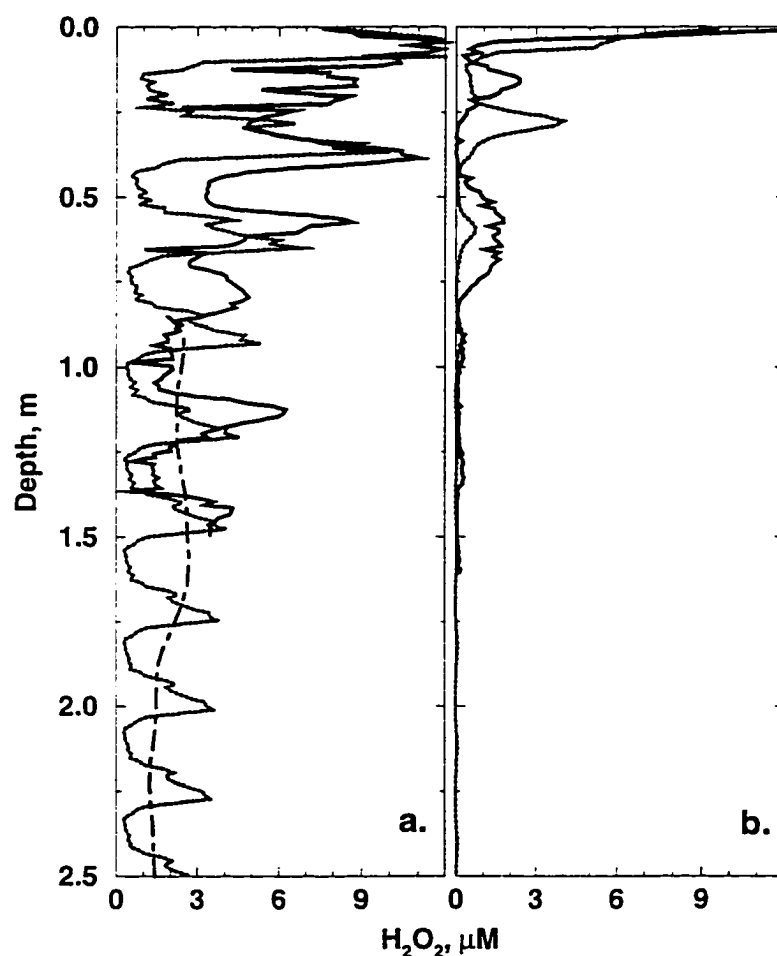


Figure 3.2: Observed snow pit (solid), firn core (dot-dash) and physically based model simulations (dot) of  $\text{H}_2\text{O}_2$  concentrations in snow and firn at (a) South Pole and (b) Siple Dome, Antarctica. In the simulations, annual accumulation was replicated from year to year and distributed uniformly throughout the year so individual summer peaks and winter troughs in the model results will not coincide with observations. Trends in observed and simulated concentration changes with depth are well matched at both sites, indicating that the physically based transfer model has wide applicability.

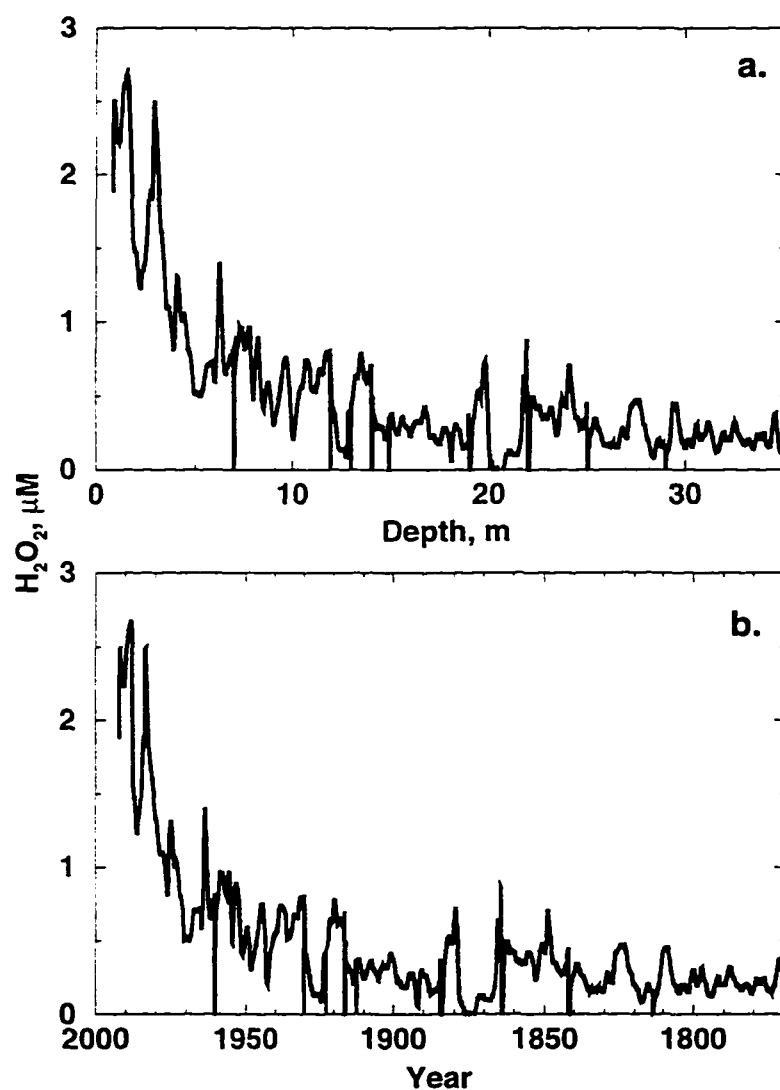


Figure 3.3: Preliminary firn core concentrations of  $\text{H}_2\text{O}_2$  at South Pole plotted against (a) depth and (b) time. Note the strong decrease in concentration to about 5 m, followed by a slower decline to  $\sim 13$  m. The time of rapid change coincides with the development of the stratospheric ozone hole over Antarctica that began in the early 1970s.

## **Appendix A**

### **A Lumped Parameter Model for the Atmosphere-to-Snow Transfer Function for Hydrogen Peroxide**


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October 13, 1997

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## A Lumped Parameter Model for the Atmosphere-to-Snow Transfer Function for Hydrogen Peroxide

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Of the main atmospheric oxidants, only hydrogen peroxide ( $H_2O_2$ ) is preserved in polar ice cores. To make use of the peroxide record, however, requires a quantitative understanding of the "transfer function" or relation between atmospheric concentrations of  $H_2O_2$  and those preserved in the ice core. Snow-pit  $H_2O_2$  profiles adjacent to three automatic snow-depth gages from Summit, Greenland were used to estimate parameters and evaluate the performance of a lumped parameter model to relate concentrations in the atmosphere with those in surface snow and shallow firn. Three of the model parameters define an equilibrium partitioning coefficient between snow and atmosphere as a nonlinear function of depositional temperature. Model parameters yielded a function that closely matched previous laboratory estimates [Conkka *et al.*, 1993]. A fourth parameter reflects the disequilibrium that may be preserved during periods of rapid accumulation. The final model parameter describes the exchange of  $H_2O_2$  between near-surface snow and the atmosphere, allowing already buried snow to either take up or release  $H_2O_2$  as conditions in and above the snowpack change. We simulated snow pit profiles by combining this transfer function model with a finite-difference model of gas-phase diffusion in the snowpack. Two applications for this transfer function are (1) to estimate the local seasonal or annual atmospheric  $H_2O_2$  concentration in the past from snow-pit and ice-core records and (2) to invert snow-pit and ice-core  $H_2O_2$  profiles to obtain estimates of the seasonal or annual accumulation time series. In the first case, an independent estimate of snow accumulation is needed, and in the second application, an independent estimate of the annual  $H_2O_2$  atmospheric cycle is needed.

### INTRODUCTION

Knowledge of the oxidizing capacity of the atmosphere, primarily a function of the atmospheric concentrations of ozone, hydroxyl radical, and hydrogen peroxide ( $H_2O_2$ ), is an important key to understanding past and future global climate change. Of these primary oxidants, only  $H_2O_2$  is archived in polar ice cores. To make use of the ice-core record as a data constraint for atmospheric photochemical modeling, however, requires a detailed, quantitative understanding of the transfer function relating the atmospheric concentration to that in the firn and ultimately the ice core [Thompson, 1995]. The incorporation of  $H_2O_2$  into firn is reversible, making the transfer function a nonlinear function of temperature, snow accumulation, and the extent of postdepositional air-snow exchange.

Seasonality in the ice-core preservation of various chemical species is well known. Numerous authors have discussed the seasonal dependence of  $\delta^{18}O$ , which is thought to be primarily related to the evaporation and condensation history of water and is taken as a marker for climatic temperature [Ciais *et al.*, 1995]. Sigg and Neftel [1988] among others have discussed the marked seasonality of  $H_2O_2$ . Beer *et al.*

[1991] evaluated the seasonal variation of a number of chemical species ( $^{10}Be$ ,  $Cl^-$ ,  $SO_4^{2-}$ ,  $H_2O_2$ ,  $^{210}Pb$ , mineral dust, and  $\delta^{18}O$ ) in a snow pit at Dye 3, Greenland. Quantitative interpretation of ice-core records spanning multiple years to centuries is particularly uncertain for seasonally dependent chemical species since the variance associated with the annual cycle is generally far greater than any expected climatic variation with time [Steig *et al.*, 1994]. Hence a single- or multiple-year deviation in a species such as  $H_2O_2$  or  $\delta^{18}O$  may be nothing more than a relatively minor shift in seasonal accumulation patterns.

If the atmosphere-snow transfer function is known, then ice-core records can be inverted to give the atmospheric  $H_2O_2$  concentration at the time of snow accumulation. Conversely, for a strongly seasonally dependent chemical species such as  $H_2O_2$ , the transfer function can be used to invert the  $H_2O_2$  profile with depth into an estimate of the snow accumulation pattern at the particular pit or core location, if assumptions about the atmospheric  $H_2O_2$  concentration and temperature histories are made. This inversion to accumulation history would allow the accumulation at the ice-core location to be deconvolved from the overall ice-core record.

We have developed a five-parameter model for the  $H_2O_2$  transfer function and used 1 year of data from three snow pits and automatic snow-depth gages (ADG) to estimate parameters and evaluate model performance. It was our hypothesis that given the timing of snow accumulation, air temperature, and atmospheric concentration of  $H_2O_2$  during the year, a relatively simple five-parameter model would be adequate to simulate concentrations of  $H_2O_2$  in near-surface

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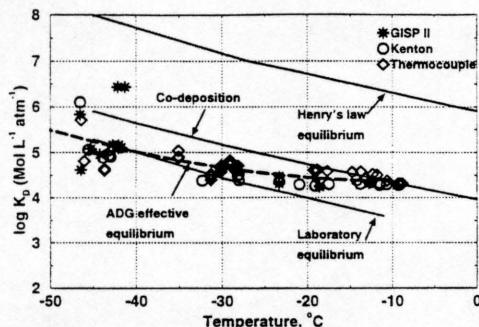


Fig. 1. The atmosphere-snow log concentration ratios for  $\text{H}_2\text{O}_2$  from the three pits as a function of temperature at the time of accumulation. The "ADG effective equilibrium" is a best fit to these data. The laboratory equilibrium line is a fit to measurements reported by Conklin *et al.* [1993]; the codeposition and Henry's law ( $K_H$ ) lines are calculated.

snow and buried snow/firn.

#### MODEL

Our snowpack model includes (1) a transfer-function component to relate atmospheric  $\text{H}_2\text{O}_2$  concentrations to those in surface and near-surface snow/firn and (2) a vapor-diffusion component to simulate diffusional redistribution deeper in the firn, down to the depth of pore close off.

##### Five-Parameter Transfer Function Model

Previous workers have argued that  $\text{H}_2\text{O}_2$  in fresh snow is either deposited according to codeposition (Figure 1) if condensation takes place in the gas phase or according to Henry's law equilibrium if  $\text{H}_2\text{O}_2$  is scavenged by liquid particles (e.g., rime formation) [Sigg and Neftel, 1988]. Codeposition refers to equal rate of condensation of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$ , resulting in the same molar ratio in frozen precipitation as in the air. Differences in sticking coefficients can also be included [Bales and Choi, 1996]. Immediately after formation,  $\text{H}_2\text{O}_2$  is released from the solid particles since such high concentrations are not stable in solid ice [Bales *et al.*, 1995b]. Laboratory studies by Conklin *et al.* [1993] showed that the equilibrium uptake capacity of snow for  $\text{H}_2\text{O}_2$  was approximately exponentially related to temperature (Figure 1) over the range of temperatures typical of Summit (-60 to -10 °C). Hence, if fresh snow is buried rapidly, then its snow-atmosphere  $\text{H}_2\text{O}_2$  concentration ratio should be somewhere between the Henry's law condition ( $K_H$ ) and the laboratory equilibrium ( $K_D$ ) [Bales *et al.*, 1995a]. It should be below the codeposition condition since concentrations above codeposition would be highly unstable and, for most of the year, precipitation is thought to form in the gas phase with only a minor (albeit important) contribution from rime [Borys *et al.*, 1991; Fuhrer *et al.*, 1996]. The exact concentration ratio preserved in the snow immediately after burial, then, is a function of not only the season and temperature but also the precipitation type (formation in the liquid or gas phase), the rate of release of  $\text{H}_2\text{O}_2$  from the snow or ice crystal (which may be affected by grain size and changes

in grain surface area during snow metamorphism), and the burial rate.

In the five-parameter model proposed here, we use a quadratic, three-parameter relation to describe the temperature-dependent relation between snow and air concentrations of  $\text{H}_2\text{O}_2$  at equilibrium:

$$\log_{10} \frac{C_{\text{snow}}}{C_{\text{air}}} = AT^2 + BT + C \quad (1)$$

where  $C_{\text{snow}}$  is the equilibrium concentration (moles per liter) of  $\text{H}_2\text{O}_2$  in surface snow,  $C_{\text{air}}$  is the concentration (atmospheres) of  $\text{H}_2\text{O}_2$  in the air in contact with the snow, and  $T$  is the surface temperature (degrees Celsius). To our knowledge, the air temperature to surface snow temperature relation is not well known so surface temperature,  $T$ , is taken to be the air temperature at 2 m. Equilibration involves  $\text{H}_2\text{O}_2$  partitioning into the bulk ice and accumulation at the grain-surface, with bulk partitioning being dominant.

In the snowpack, however, equilibrium with the atmosphere may not have been reached, since after the snow has been buried only limited exchange with the atmosphere is possible. To allow for preservation of the snow prior to it reaching equilibrium with the atmosphere, we define a simple disequilibrium relationship that is a linear function of the deposition rate:

$$Q = 1.0 + \frac{dz}{dt} S_{eq} \quad (2)$$

where  $dz/dt$  is accumulation rate in meters per year, and  $S_{eq}$  is the parameter that describes the sensitivity to deposition rate. This factor  $Q$  is used to modify the snow-atmosphere  $\text{H}_2\text{O}_2$  partitioning ratio:

$$\left( \frac{C_{\text{snow}}}{C_{\text{air}}} \right)_{\text{effective}} = Q \left( \frac{C_{\text{snow}}}{C_{\text{air}}} \right)_{\text{equilibrium}} \quad (3)$$

$Q$  is only applied to the surface layer of snow, before it is buried by subsequent snowfall.

When the accumulation rate is very low, the effective and equilibrium concentration ratios are equivalent. Conversely, for very high accumulation rates, the effective log concentration ratio can be significantly larger. Note that on the equilibrium versus temperature diagram (Figure 1), the effective equilibrium line will simply shift up by  $\log Q$  for the case with a constant accumulation rate.

Interaction of the atmosphere with buried snow is well known, and formal analyses of postdepositional changes and burial rates have been made [Bales and Choi, 1996; Davis *et al.*, 1996; Waddington *et al.*, 1996]. We use the final parameter in the transfer-function model to describe the bulk interaction of near-surface snow with the atmosphere above. This single term reflects the net impact of near-surface metamorphic process and wind mixing of surface snow layers, as well as advection and diffusion of high-concentration air into the snowpack in summer and low-concentration air in winter. This can be written as

$$C_{i,t} = MC_{i,0,t} + (1 - M)C_{i,t-1} \quad (4)$$

where  $C_{i,t}$  is the effective snow equilibrium concentration of  $\text{H}_2\text{O}_2$ ,  $i$  is the layer number (relative to the surface layer

at  $i = 0$ ,  $t$  is the time step associated with the current surface layer, and  $M$  is the fraction of the current surface equilibrium condition ( $C_{i=0,t}$ ) in the current concentration of a buried layer ( $C_{i,t}$ ). We assume that such interaction decreases exponentially with depth, and to allow more exchange when snow stays at the same depth for long periods of time, the exposure time ( $t_i$ ) or time before the next layer accumulates is included. Thus the impact  $M$  of the current atmospheric concentration on a buried layer can be described as

$$M = \exp\left(\frac{-z_i}{t_i z_{\text{efold}}}\right) \quad (5)$$

where  $z_i$  is the buried layer depth relative to the surface and  $z_{\text{efold}}$  (meters per year) determines the  $e$ -folding depth of the surface impact for a given exposure time  $t_i$ .  $E$ -folding depth is the depth divided by the exposure time when the value of  $M$  is  $1/e$  or 0.37. Note that, unlike  $Q$ , the surface interaction described by  $M$  takes place after burial. Note that time-dependent, physical characteristics other than exposure time may also be included in this term (e.g., windiness, surface roughness) if they are thought to have an impact on the degree of interaction of surface conditions with the buried near-surface layers.

#### Vapor-Diffusion Model

After burial of snow, hydrogen peroxide undergoes diffusional redistribution with summer-related peak values decreasing and winter-related troughs increasing [Sigg and Neftel, 1988]. We use a "retarded-diffusion" model based on Fick's law to describe the smoothing of  $\text{H}_2\text{O}_2$  in the firn [Bales et al., 1987; Whillans and Grootes, 1985]. The effective gas-phase diffusion coefficient is lower than the molecular-diffusion coefficient to account for retardation caused by retention of the diffusing gas in the ice. Whillans and Grootes [1985] demonstrated that diffusion in the open pore space was the rate limiting step in  $\delta^{18}\text{O}$  diffusion and so computed the diffusivity of  $\delta^{18}\text{O}$  as a function of the partial pressure of water vapor over ice and the fraction of the air in the bulk snow volume. Sigg and Neftel [1988] found through a simple analysis of the annual variance in the  $\text{H}_2\text{O}_2$  signal in recent snow and at depth with diffusion backed out that the effective diffusivity of  $\text{H}_2\text{O}_2$  is about 1.5 to 1.75 that of  $\delta^{18}\text{O}$ , reflecting a lower uptake capacity of the snow for  $\text{H}_2\text{O}_2$  than for  $\delta^{18}\text{O}$ .

We used a simple finite-difference implementation of the Whillans and Grootes [1985] model to simulate gas-phase, postdepositional diffusion in the snowpack. By repeatedly running a 100-year simulation and then comparing the resulting  $\text{H}_2\text{O}_2$  profile to that measured in the Eurocore in 1988 [Sigg and Neftel, 1988], we computed an  $\text{H}_2\text{O}_2$  to  $\delta^{18}\text{O}$  diffusivity ratio of about 1.7, consistent with the earlier estimates of Sigg and Neftel.

In the snow-pit simulations, a surface layer of snow accumulates with thickness  $z_i$  and an  $\text{H}_2\text{O}_2$  concentration consistent with the chosen model parameters  $A$ ,  $B$ ,  $C$  and  $S_{\text{eq}}$ . After accumulation, the modeled  $\text{H}_2\text{O}_2$  concentration changes according to the rate of burial, the surface conditions during the early stages of burial, and the model parameter  $z_{\text{efold}}$ . The layer compacts following the depth-density relation ob-

served on the 1993 GISP2 core (which is consistent with the spot measurements made on the Eurocore), and diffusion ensues.

A seasonal density function, exponentially damped with depth with an  $e$ -folding depth of 2 m, is superimposed on the monotonic density profile to approximate the shallow density profile observed in snow pits at Summit. The temperature of the snowpack changes with depth and season and is modeled by heat conduction into the snow, assuming a sinusoidal annual surface temperature cycle. Observations from the automatic weather stations were used to derive an annual temperature sinusoid for Summit that reaches a maximum each year on July 14 of  $-12^\circ\text{C}$  and has a mean of  $-31^\circ\text{C}$  (data not shown). The diffusivity was computed from this snowpack temperature and the modeled density. Input data include the timing of snow accumulation events, which can vary smoothly with season or sporadically from layer to layer, the (constant) layer thickness deposited in each event, the atmospheric  $\text{H}_2\text{O}_2$  concentration, and the surface air temperature during the simulation. The result is synthetic profiles with depth (or time) for  $\text{H}_2\text{O}_2$  and  $\delta^{18}\text{O}$ . Note that a constant layer thickness was used in the finite-difference implementation of diffusion; this is not a significant constraint, especially since snow pits are generally sampled in even depth intervals.

#### METHODS

Snow pits were dug at three sites where snow accumulation was recorded. Two pits were dug in June 1995 directly beneath acoustic depth gages located at the Kenton and Greenland Ice Sheet Project 2 (GISP2) automatic weather stations (AWS) [Stearns et al., 1993]. The Kenton AWS is located about 30 km to the south of the GISP2 deep drill site ( $72^\circ 58' \text{N}$ ,  $38^\circ 46' \text{W}$ ) at Summit, Greenland; the GISP2 AWS is about 1 km south of the main GISP2 camp. The third pit was dug adjacent to an array of 25 type E (0.076-mm diameter) thermocouples suspended vertically over the snow surface. The interval between each thermocouple was approximately 2.5 cm. Temperature was sampled every 3 hours using a Campbell Scientific CR10 data logger and AM25 solid state multiplexor. The data logger and multiplexor were buried in the snow 5 m from the thermocouple array. As long as a thermocouple remained above the snow surface, then the diel temperature cycle was obvious in its output. However, when buried, the diel cycle was heavily damped, thereby indicating when the snow surface had reached the thermocouple height. This pit, located about 10 m from the GISP2 AWS, was sampled in early May 1995. The pits beneath the acoustic depth gages were sampled at approximately 3-cm resolution, while the pit by the thermocouple string was sampled more finely in the shallow section and at about 3 cm spacing in the deeper section.

Snow  $\delta^{18}\text{O}$  was measured by equilibration with dry  $\text{CO}_2$  at  $15^\circ\text{C}$  using 2-mL meltwater samples in an automated  $\text{CO}_2$ - $\text{H}_2\text{O}$  equilibration unit coupled to a Delta-S gas ratio mass spectrometer.  $\text{H}_2\text{O}_2$  analyses were done as described previously [Bales et al., 1995b].



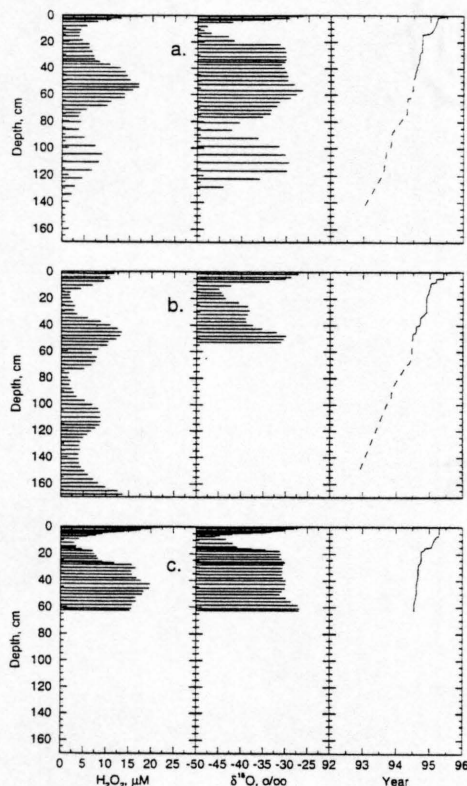


Fig. 2.  $\text{H}_2\text{O}_2$  concentrations,  $\delta^{18}\text{O}$ , and timing of accumulation from the three snow pits dug beneath ADGs at Summit, Greenland: (a) Kenton AWS, (b) GISP2 AWS, and (c) GISP2 thermocouple pits. The dashed lines represent extrapolated accumulation histories.

## RESULTS

### Field Measurements

The  $\text{H}_2\text{O}_2$  and  $\delta^{18}\text{O}$  profiles showed distinct differences between pits, with much of the difference due to when snow accumulated at each site. The measured  $\text{H}_2\text{O}_2$  and  $\delta^{18}\text{O}$  profiles for each pit showed the typical seasonal cycle, with higher values in summer and lower values in winter (Figure 2). The dates of accumulation at each depth were measured for 1994–1995 and inferred prior to summer 1994 (dashed lines), since none of the depth-measurement devices were deployed at exactly the same place for more than 1 year.

The same pit data are combined and plotted in Figure 3 against the time of year that the snow accumulated. The air temperature from the Kenton AWS is plotted along with a photochemical model estimate of the atmospheric  $\text{H}_2\text{O}_2$  concentration [Bales and Choi, 1996]. The 7-day average of the measured atmospheric  $\text{H}_2\text{O}_2$  concentrations from mid-April to mid-July 1995 is plotted with the photochemical model estimate. As reported for previous years at the same site,

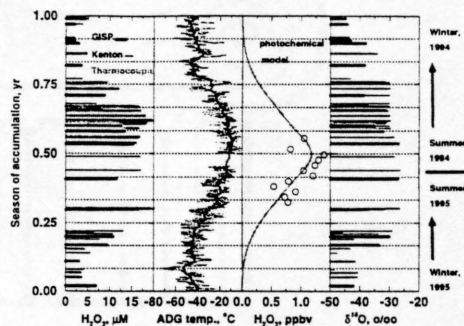


Fig. 3. Snow  $\text{H}_2\text{O}_2$  concentrations, air temperature, measured and modeled atmospheric  $\text{H}_2\text{O}_2$  concentrations, and  $\delta^{18}\text{O}$  plotted against time. Note that in order to illustrate changes over a calendar year, the field data have been split with June to December 1994 plotted on the upper half and January to June 1995 plotted on the lower half of the graph.

measured and modeled values were in approximate agreement [Bales et al., 1995; Neftel, 1996; Fuhrer et al., 1996]. Note that on a timescale, the overall shapes of the annual  $\text{H}_2\text{O}_2$  and  $\delta^{18}\text{O}$  profiles were quite similar between all three pits. One remaining difference is the higher  $\text{H}_2\text{O}_2$  values in the thermocouple string pit in late summer and early fall 1994.

The summer peaks in  $\delta^{18}\text{O}$  were much broader than those for  $\text{H}_2\text{O}_2$  and extended well into the autumn. Because the  $\text{H}_2\text{O}_2$  signal reflects both the depositional temperature and the atmospheric  $\text{H}_2\text{O}_2$  concentration, which is itself a strong function of the actinic flux, the  $\text{H}_2\text{O}_2$  maximum in the snow pit was found relatively close to the summer solstice. On the other hand,  $\delta^{18}\text{O}$  reflects the warmer conditions in autumn since it is thought to be primarily determined by precipitation temperature and, to a lesser extent, by transport.

The observed air temperature (dashed line) is plotted with the  $\delta^{18}\text{O}$  implied temperature (symbols) as a function of season on Figure 4. While the overall shape is similar in the observed and implied seasonal temperature cycles, the  $\delta^{18}\text{O}$  implied cycle is shifted to earlier time and has a lower amplitude about the mean. Both of these characteristics are consistent with postdepositional changes in  $\delta^{18}\text{O}$ , as with  $\text{H}_2\text{O}_2$ .

Using the annual atmospheric  $\text{H}_2\text{O}_2$  cycle estimated from photochemical model calculations, the observed  $\text{H}_2\text{O}_2$  concentrations from snow pits, and surface temperature, we calculated "observed" snow-atmosphere concentration ratios. These are plotted as a function of surface air temperature on Figure 1 for comparison with Henry's law, codeposition, and published laboratory equilibrium relations. While the ADG measured relation generally lies between the codeposition line and the equilibrium ( $K_D$ ) line as expected, it is clearly not linear in log-linear space, and by this simple analysis, field measurements are not in agreement with the laboratory equilibrium measurements. Two possible explanations for this discrepancy are: (1) that the snow continued to interact with the atmosphere at least for some time after



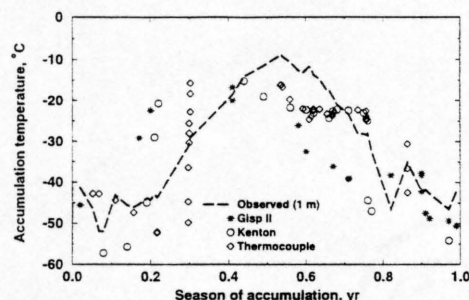


Fig. 4. Measured air temperature (dashed) and the accumulation temperature implied by the measured  $\delta^{18}\text{O}$  values in the snow pits (symbols) plotted against season of year. The  $\delta^{18}\text{O}$  temperature (degrees Celsius) is calculated using the following relation given by Cuffey *et al.* [1992]:  $T = (\delta^{18}\text{O} + 18.2)/0.53$ , where  $\delta^{18}\text{O}$  is in per mil.

burial and (2) that the snow had not yet reached equilibrium when it was buried and closed off from contact with the atmosphere [Bales *et al.*, 1995a].

#### Model Fits

The measured  $\text{H}_2\text{O}_2$  concentration, accumulation timing, and accumulation temperature from the thermocouple string pit (Figure 2c) were used in a systematic search routine to estimate parameter values for the five-parameter transfer-function model. We chose a simple root means square (RMS) error between the target (observed) and modeled snow pit  $\text{H}_2\text{O}_2$  profile as the objective function to be minimized. Note that the objective function has units of concentration.

The optimized parameters were 3.12, -0.035, 0.00025, 0.72, and 1.05 for  $A$ ,  $B$ ,  $C$ ,  $z_{efold}$ , and  $S_{eq}$  respectively. Selected orthogonal objective function surfaces at the minimum are shown in Figures 5a-5d. Note the well-defined minima and relatively smooth error surfaces. Note also that many of the parameters are interdependent, so the optimization must be carried out for all five parameters simultaneously. The temperature-dependent snow-atmosphere relations defined by parameters  $A$ ,  $B$ , and  $C$ , labeled "thermocouple optimization" (Figure 6), are in excellent agreement with the laboratory equilibrium line.

The long trough in the objective function surface (e.g., Figure 5a) indicates that the uptake capacity with temperature parameters are interdependent. Hence there is little difference in the RMS error between the modeled and observed profiles for  $B = 0.4$ ,  $C = 3.0$  and  $B = 0.0$ ,  $C = 3.75$ . A similar interdependence can be found between the intercept term,  $C$ , and the disequilibrium term,  $S_{eq}$  (Figure 5b). These troughs, however, define a family of curves that all have very nearly the same slope within the temperature range -10 to -45 °C. This slope is essentially parallel to that found in the published laboratory work. The intercept,  $C$ , is highly dependent on the lowest temperature values because (1) the deposition rate is lowest for these values and (2) the disequilibrium term is positive so the thermodynamic equilibrium concentration ratio must always be less than the effective ratio (equation (3)). Unfortunately, these low-

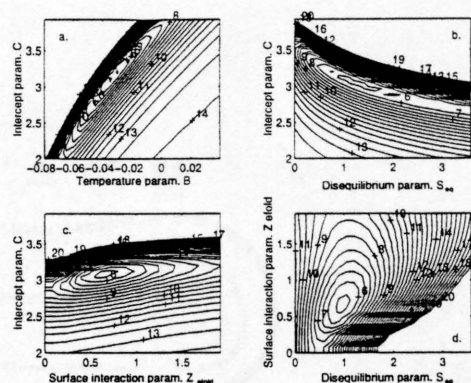


Fig. 5. Selected orthogonal objective function surfaces from the five-parameter transfer-function model optimization using the thermocouple-string pit data.

temperature values have the greatest uncertainty since confidence in the timing of the accumulation is lowest in winter. This is due to the much smaller diel temperature cycle for the thermocouple string pit and because the acoustic depth gages tend to perform poorly in midwinter when the sensors get encrusted with blowing snow. Also, the modeled atmospheric  $\text{H}_2\text{O}_2$  concentration is very low, making the ratio of snow to atmospheric concentration more sensitive to error. In addition, long-range transport of  $\text{H}_2\text{O}_2$ , which is small relative to the in situ photochemical production in the atmosphere over Summit in summer, is much more important in winter when the in situ production is essentially absent. The modeled atmospheric concentration used in this study did not include a long-range transport term. As demonstrated in Figures 5c and 5d, there is far less interdependence between the surface interaction parameter  $z_{efold}$  and the uptake capacity parameters  $A$ ,  $B$ , and  $C$  and the disequilibrium parameter  $S_{eq}$ .

To test the generality of the parameters estimated from the thermocouple string pit, additional optimizations were made using the two acoustic depth gage pits. For these cases, the surface interaction and disequilibrium terms were fixed at  $z_{efold} = 0.72$  and  $S_{eq} = 1.05$  since we had the most confidence in the depth-accumulation date relationship for the thermocouple pit. The resulting uptake capacity relationships are plotted in Figure 6 as "Kenton optimization" and "GISP optimization." Again, note the excellent agreement between the GISP2, thermocouple and laboratory equilibrium relationships, although the Kenton estimate was not as consistent.

The modeled snow-pit profiles for  $\text{H}_2\text{O}_2$  using the parameters estimated from the thermocouple pit are shown in Figure 7. The overall shapes are similar for the Kenton and thermocouple pits but differ for the GISP2 pit. As can be seen in Figures 2a-2c, the GISP2 accumulation history had marked differences from the thermocouple and Kenton pits.

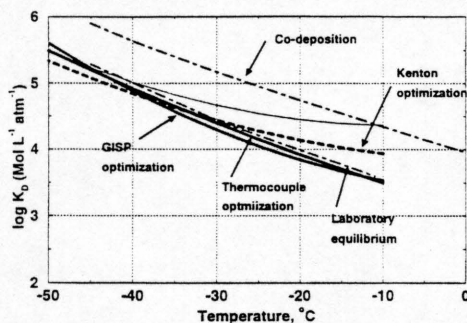


Fig. 6. Log concentration ratios for  $\text{H}_2\text{O}_2$  as a function of temperature resulting from parameter estimation using the automatic depth gage snow-pit data. For all three cases, the surface interaction ( $z_{\text{fold}}$ ) and disequilibrium terms ( $S_{\text{eq}}$ ) were  $0.72 \text{ m yr}^{-1}$  and  $1.05 \text{ yr m}^{-1}$  respectively. Laboratory equilibrium, codeposition, and ADG effective equilibrium lines are from Figure 1.

#### DISCUSSION

In our five-parameter model, we assumed that pit-to-pit differences in  $\text{H}_2\text{O}_2$  concentrations versus time (Figure 3) were the result of different accumulation rates and thus varying degrees of (incomplete) equilibration of buried layers with the atmosphere. It was assumed that all of the pits experienced the same depositional temperatures and atmospheric  $\text{H}_2\text{O}_2$  concentrations throughout the year. There is a strong positive correlation between accumulation rate and  $\text{H}_2\text{O}_2$  concentration; that is, a short-term increase in accumulation rate leads to a short-term increase in preserved  $\text{H}_2\text{O}_2$ , which strongly supports the idea that the snow is preserved out of thermodynamic equilibrium (e.g., Figure 2c). This relationship is also seen to a lesser degree in the  $\delta^{18}\text{O}$  profile and suggests a transfer function for  $\delta^{18}\text{O}$  that is to some degree a function of accumulation rate. For ice cores we must rely on  $\delta^{18}\text{O}$  implied temperatures to interpret the  $\text{H}_2\text{O}_2$  profile, so understanding any  $\delta^{18}\text{O}$  transfer function is of utmost importance also.

While effects of both the surface interaction and disequilibrium terms depend on how the deposition rate varies both

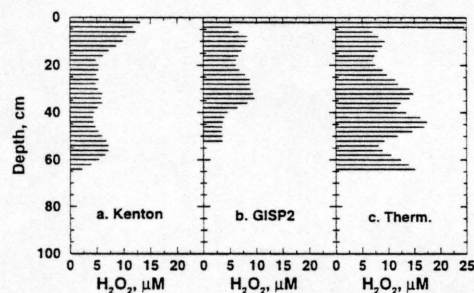


Fig. 7. Modeled  $\text{H}_2\text{O}_2$  profiles with depth for the three ADG pits: (a) Kenton AWS, (b) GISP2 AWS, and (c) GISP2 thermocouple pits.

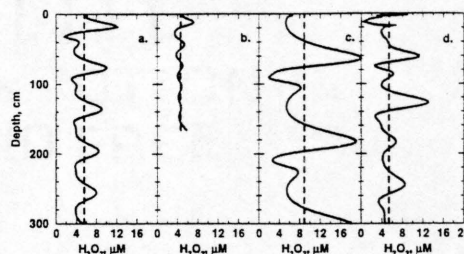


Fig. 8. Example synthetic snow-pit  $\text{H}_2\text{O}_2$  profiles with various accumulation histories: (a) uniform at  $60 \text{ cm yr}^{-1}$ , (b) uniform at  $30 \text{ cm yr}^{-1}$ , (c) uniform at  $120 \text{ cm yr}^{-1}$ , and (d) sporadic around  $60 \text{ cm yr}^{-1}$ . The dashed line is the pit average concentration.

throughout the year and between sites, some insight into the physical meaning of the parameter values can be gained using the average accumulation rate at Summit of about  $0.6 \text{ m yr}^{-1}$ . For a 30 layer per year model ( $t_i = 0.033 \text{ years}$ ), the average  $e$ -folding depth of surface interaction when  $z_{\text{fold}} = 0.72 \text{ m yr}^{-1}$  is  $0.024 \text{ m}$ . Similarly, the average value for  $Q$  when  $S_{\text{eq}} = 1.05 \text{ yr m}^{-1}$  is  $1.64$ , representing a  $0.21$  shift upward in the effective log concentration ratio to temperature relation (Figure 6). From Figure 1, the concentration at codeposition would be about  $5.6$  times that at equilibrium. On average, snow formed by codeposition has released about  $85\%$  of the excess  $\text{H}_2\text{O}_2$  when  $Q = 1.64$  and  $t_i = 0.033 \text{ y}$ . Laboratory studies show that, at  $-15^\circ\text{C}$ , snow will release about  $85\%$  of its excess  $\text{H}_2\text{O}_2$  after  $0.033 \text{ y}$ . Note that the majority of the snow represented in the pits accumulated when air temperatures were about  $-15^\circ\text{C}$  (Figure 3). Therefore, if deposition is more rapid in the summer and fall, as it was during the 1994-1995 period at Summit, then buried summer and fall snow is strongly out of equilibrium and winter snow is closer to equilibrium. The result is a highly nonlinear shape of the "ADG effective equilibrium" line, as on Figure 1.

To investigate the sensitivity of the final preserved  $\text{H}_2\text{O}_2$  profile to the timing of snow accumulation, model snow pits were constructed using the optimum parameters listed above for a number of deposition sequences (Figure 8). First, note the major spring and minor fall maxima in the uniform deposition case for Summit conditions (Figure 8a). While the surface interaction term tends to make the preserved  $\text{H}_2\text{O}_2$  profile less sensitive to accumulation timing, the disequilibrium term greatly enhances this sensitivity. Hence, halving the uniform deposition rate (Figure 8b) resulted in far smaller annual cycles and a  $20\%$  lower average concentration.

Doubling the uniform deposition rate (Figure 8c) greatly enhanced the annual cycles because of both enhanced disequilibrium and less diffusional redistribution and also increased the average preserved  $\text{H}_2\text{O}_2$  concentration by  $50\%$ . Sporadically varying accumulation (Figure 8d) resulted in a much less uniform  $\text{H}_2\text{O}_2$  profile with fall minima sometimes preserved and much greater variance in the amplitudes of the spring maxima but little change in the average concentration preserved.

The modeled pit reflects the patterns observed in the thermocouple and Kenton pits better than for GISP2. Since snow accumulation was approximately coincident for the thermocouple and Kenton, then seasonality in the parameters  $S_{eq}$  and  $Z_{efield}$  would not be distinguishable. GISP2, on the other hand, had far more accumulation in winter and far less in the fall. Hence the difference in fit may be caused by seasonality in these two parameters. That is, grain size and/or snow recrystallization rate may be different in the summer half of year, leading to a different  $S_{eq}$  for winter snow than for summer snow. The GISP2 pit may be overly sensitive to deposition rate in winter.

Application of this model to infer past atmospheric  $H_2O_2$  concentrations from those in the ice-core record will require an independent estimate of the timing of snow accumulation. Attempts to estimate the timing of accumulation at ice-core locations such as Summit, Greenland, have been made, although they have generally relied on relatively low spatially resolved and recent records such as passive microwave remote-sensing data [Shuman *et al.*, 1995] or synoptic-scale meteorological information [Bromwich *et al.*, 1993] coupled to snow-pit or surface observations for calibration. However, as is demonstrated by the strong variability in chemical-species depth profiles in snow-pits collected at the same time and within a few kilometers of each other, the correspondence between the regional-accumulation pattern and that at a point is often quite low. Other authors have used snow-pit stratigraphy [Alley *et al.*, 1990; Gow, 1965], as a means of estimating accumulation timing. These studies rely primarily on hoar layers and so are generally limited to defining late spring to early fall marker horizons.

Estimating accumulation timing using known transfer functions to invert chemical records has the advantage of being specific to the individual pit or ice-core location and it can be extended back in time to preindustrial conditions or even earlier. Seasonally varying chemical species such as  $Ca^{2+}$ ,  $NH_4^+$ ,  $NO_3^-$ , and methanesulphonate (MSA) could be used to estimate the timing of snow accumulation, assuming the seasonal pattern of relative atmospheric concentrations for each species is known.  $Ca^{2+}$ ,  $NH_4^+$ , and MSA are aerosol-associated species, transported to an ice-core site from lower latitudes, and once deposited are relatively immobile in the snow/firn. Concentrations deposited in the snow depend largely on atmospheric concentrations rather than on temperature.  $NO_3^-$  undergoes some postdepositional exchange, but seasonal patterns are still relatively preserved. Obviously, if more chemical species are used, there will be more confidence in the accumulation estimate. The  $\delta^{18}O$  is needed for its temperature record but can also provide an indication of the seasonality of accumulation.

In periods with a known or relatively constant annual atmospheric  $H_2O_2$  concentration,  $H_2O_2$  can be used to reconstruct the accumulation history.  $H_2O_2$  should be better than the other species noted above because of its distinct seasonal cycle. While subseasonal resolution is possible in situations where the annual  $H_2O_2$  cycle is preserved, it may also be possible to identify and deconvolve multiyear accumulation seasonality shifts in situations where the seasonal  $H_2O_2$  cycle does not survive diffusional smoothing. For coupled  $H_2O_2$  and  $\delta^{18}O$  profiles, the annual cycles are in phase

so that changes in accumulation timing would result in approximately coincident increases or decreases of both signals. Conversely, climatic cooling would result in higher preserved  $H_2O_2$  (Figure 1) and lower  $\delta^{18}O$  for a negatively correlated relationship.

#### CONCLUSIONS

Because the log concentration ratio estimated in the optimization is an equilibrium relationship, it should apply to all polar sites. The disequilibrium parameter and especially the surface interaction parameter, however, depend on precipitation characteristics, grain size, solar radiation, wind, surface roughness, and other site-specific features. While parameter estimation using only one record from one site yielded a temperature-dependent snow uptake capacity for  $H_2O_2$  that is in excellent agreement with previous laboratory work, there is clearly a need for more such data sets both from Summit and from other areas. Data from polar sites with different temperature ranges (e.g., south pole) would better define this relationship although our current success in matching the laboratory-determined  $K_D$  will allow constraint of that function and focusing future evaluations on the disequilibrium parameters. ADG pit profiles longer than 1 year in duration would allow much better parameterization of the surface interaction term, and year-round surface samples and micropits would result in better definition of the disequilibrium term. The still large RMS error of approximately  $5 \mu M$  between the modeled and observed snow-pits indicates that (1) finer-resolution sampling of snow-pits and more closely spaced thermocouples would reduce uncertainty of parameter estimation and (2) an additional model term or terms, e.g., to capture effects of wind, may be necessary. Future model development will focus on improving the agreement between the modeled and observed profiles by (1) incorporating physically based grain size and temperature effects into the surface interaction and disequilibrium parameters and (2) decoupling the surface interaction and disequilibrium time steps from the inpack vapor diffusion time step so that snow deposition and subsequent removal by wind scouring is better simulated in the model. The latter change is particularly important for modeling pits in sites with low and highly variable accumulation rates such as south pole.

By coupling process-level models of specific physical phenomena (e.g., wind pumping) with this type of lumped parameter model that is parameterized directly by field data, we hope to improve our understanding of the overall atmosphere-to-snow transfer process for  $H_2O_2$  and other reversibly deposited chemical species. A quantitative understanding of the transfer function will make possible estimates of the timing of snow accumulation in ice-cores and so improve interpretation of all seasonally dependent chemical species. Moreover, the transfer function for  $H_2O_2$  will make possible inversion of ice-core records to local  $H_2O_2$  atmospheric concentrations and thus provide more reliable constraints for modeling changes in the global atmospheric oxidation capacity.

Finally, a multispecies ice-core record with subannual resolution reaching at least back to preindustrial times is needed to test the model's ability to invert an ice-core  $H_2O_2$  record.

**Acknowledgments.** This work was supported by National Science Foundation grant OPP-9224192 and a NASA Graduate Fellowship for Global Change (NGT 30269). We also acknowledge the cooperation of A. Long and use of resources in the University of Arizona's Laboratory of Isotope Geochemistry for doing  $\delta^{18}\text{O}$  analyses.

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## **Appendix B**

### **Physically Based Modeling of Atmosphere-to-Snow-to-Firn Transfer of $\text{H}_2\text{O}_2$ at South Pole**

## **Physically Based Modeling of Atmosphere-to-Snow-to-Firn Transfer of H<sub>2</sub>O<sub>2</sub> at South Pole**

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Short title: TRANSFER MODELING OF H<sub>2</sub>O<sub>2</sub> AT SOUTH POLE

**Abstract.** Quantitative interpretation of ice core chemical records requires a detailed understanding of the transfer processes that relate atmospheric concentrations to those in the snow, firn, and ice. A unique, 2 year set of year round surface snow samples at South Pole and snow pits, with associated accumulation histories, were used to test a physically based model for atmosphere to firn transfer of  $\text{H}_2\text{O}_2$ . The model, which extends our previous transfer modeling at South Pole into the snow pack, is based on the advection-dispersion equation and spherical diffusion within representative snow grains. Required physical characteristics of the snow pack, such as snow temperature and ventilation, were estimated independently using established physical models. The surface snow samples and related model simulations show that there is a repeatable annual cycle in  $\text{H}_2\text{O}_2$  in the surface snow at South Pole. It peaks in early spring and surface snow concentration is primarily determined by atmospheric concentration and temperature, with some dependence on grain size. The snow pits and associated model simulations point out the importance of accumulation timing and annual accumulation rate in understanding the deposition and preservation of  $\text{H}_2\text{O}_2$  and  $\delta^{18}\text{O}$  at South Pole. Long term snow pack simulations suggest that the firn continues to lose  $\text{H}_2\text{O}_2$  to the atmosphere for at least 10-12 years ( $\sim 3$  m) after burial at current South Pole temperatures and accumulation rates.



## Introduction

The oxidizing capacity of the atmosphere, primarily determined by concentrations of ozone, hydroxyl radical, and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), is important in understanding global climate change because it determines the atmospheric lifetimes of most trace gases. Models for investigating changes in atmospheric oxidation capacity, however, require historical data for validation [Thompson, 1992]. Ice cores provide a detailed record of past changes in atmospheric chemistry and meteorology, although of the three primary oxidants, only  $\text{H}_2\text{O}_2$  is preserved. Quantitative interpretation of an ice core record requires detailed understanding of the physical transfer processes that relate atmospheric chemical concentrations to those found in surface snow, firn, and ice [Neftel, 1996; Wolff, 1996].

Unlike aerosols, volatile species such as hydrogen peroxide, formaldehyde, and organic acids are reversibly incorporated in the snow because a fraction of the deposited mass of these species cycles between the atmosphere and snow as precipitation ages and as surface and near-surface conditions change [Bales *et al.*, 1992; McConnell *et al.*, 1997c].  $\text{H}_2\text{O}_2$ , which is important because of its photochemical role, has been relatively well studied and is also seen as a good model compound for understanding reversible deposition in general [Bales and Wolff, 1995].

Models of chemical transfer, or transfer functions, are most readily formulated in the forward direction, i.e., atmosphere-to-snow-to-firn-to-ice, and can help lead to an understanding of the underlying physical processes [Waddington, 1996; McConnell *et al.*, 1997c]. In an example of a forward model, McConnell *et al.* [1996b] developed a lumped-parameter model to simulate  $\text{H}_2\text{O}_2$  concentrations in a snow pit given photochemical modeled estimates of the atmospheric concentration of  $\text{H}_2\text{O}_2$  and a priori knowledge of the timing of snow accumulation from automatic depth gauges. The empirical model was used to simulate three snow pits at Summit, Greenland, each spanning the same period of summer, 1994 to summer, 1995. To define model parameters, simulations were objectively compared to the three pit concentration



profiles. The results indicated that the preserved  $\text{H}_2\text{O}_2$  profile is strongly dependent on snow accumulation rate and timing but the model was not able to simulate pits adequately with different accumulation histories without modifying the empirical parameters. That is, the empirical parameters were not general.

The interpretation of an ice core record requires inverse, rather than forward modeling, i.e., ice-to-firn-to-snow-to-atmosphere. *McConnell et al* [1997c] used a set of year round surface snow scrapes to test a physically based model for atmosphere-to-snow transfer and, by inversion of the surface snow record, were able to estimate the annual cycle in atmospheric  $\text{H}_2\text{O}_2$  at South Pole. By restricting the inversion to surface snow samples and making the assumption that snow at the very near surface was “old” snow, they avoided both the non-linearities in the time-depth relationship and unknown accumulation events. They also avoided those processes active beneath the snow surface, e.g., diminished exchange during burial, redistribution of  $\text{H}_2\text{O}_2$  by vapor phase diffusion in the snow pack. Before attempting the more complete inverse modeling of buried snow and firn, the forward processes of atmosphere-to-snow-to-firn-to-ice transfer must be better understood.

In this study, we developed a physically based, forward model for atmosphere-to-snow-to-firn transfer that extends our previously reported model for atmosphere-to-snow transfer down into the snow pack [*McConnell et al.*, 1997c]. The model, which is based on the advection-dispersion equation and includes spherical diffusion within the snow grains, simulates a snow pack concentration profile for  $\text{H}_2\text{O}_2$  given time series of atmospheric  $\text{H}_2\text{O}_2$ , air temperature, snow pack temperature with depth, ventilation characteristics with depth, and accumulation history. To test the model, we used a unique, weekly set of surface snow samples collected year round at South Pole, as well as 4 snow pit concentration profiles collected at South Pole in January, 1996.

## Methods

Field sampling at South Pole was designed to focus on individual components of the transfer process. For example, surface snow scrapes were collected year round to focus on rapid cycling of  $\text{H}_2\text{O}_2$  between atmosphere and very near-surface snow and short-term atmospheric measurements of  $\text{H}_2\text{O}_2$  were made in order to calibrate photochemical modeling.

### Year Round Surface Snow Samples

Surface snow samples were collected approximately once a week by NOAA winter-over staff in the Clean Air Sector at South Pole. Samples were taken from December, 1994 through December, 1997. To mitigate spatial variability, each surface sample consisted of six individual surface snow scrapes with an average water-equivalent depth of about  $0.05 \text{ g cm}^{-2}$ . When sampling in the presence of a strong vertical gradient, detailed knowledge of sample depth is critical. The surface scrapes samples were aliquoted individually at South Pole and then re-frozen for eventual analysis for  $\text{H}_2\text{O}_2$  and  $\delta^{18}\text{O}$  at our lab in Tucson.  $\text{H}_2\text{O}_2$  concentration was determined using the peroxidase-based fluorescence method [Sigg *et al.*, 1992].  $\delta^{18}\text{O}$  was measured by equilibrium with dry  $\text{CO}_2$  at  $15^\circ\text{C}$  using 2-ml meltwater samples in an automated  $\text{CO}_2 - \text{H}_2\text{O}$  equilibration unit coupled to a Delta-S gas ratio mass spectrometer.

### Snow Pits at Accumulation Stakes

Snow pits were sampled at 1 cm vertical resolution, the samples aliquoted and re-frozen on site and then returned to Tucson for  $\text{H}_2\text{O}_2$  and  $\delta^{18}\text{O}$  analyses. The pits were located about 500 m from the Amundsen-Scott Station (Figure 1), adjacent to poles that are part of a long-term, snow accumulation stake array [McConnell *et al.*, 1997a]. Only stakes around the perimeter of the accumulation array were considered as possible sampling sites in order to have as little impact on the

long-term accumulation record as possible. After analyzing the year round, monthly accumulation data, pits at four stakes were selected to give minimum (stakes 31 and 01) and maximum (stake 06) variance in monthly accumulation about the mean over the 7.25 yr continuous record. An additional stake (stake 10) was selected because it showed maximum accumulation in the month just prior to sampling (Figure 2).

### Short-Term Atmospheric H<sub>2</sub>O<sub>2</sub> Measurements

Two short-term periods of atmospheric H<sub>2</sub>O<sub>2</sub> measurements were made in November/December, 1994 and January, 1996 [McConnell *et al.*, 1997c]. Intakes were located near the Clean Air Facility at a height of ~2 m. The continuous gas-phase detector was described in Bales *et al.* [1995].

### Models

To model atmosphere-to-snow-to-firn transfer processes requires time series of a number of variables that are difficult, if not impossible, to measure year round. Thus, separate models were used to estimate 1) the atmospheric concentration of H<sub>2</sub>O<sub>2</sub>, 2) the ventilation characteristics of the snow pack, and 3) the snow temperature with depth. In addition, we used previously reported modeling and laboratory values for 1) H<sub>2</sub>O<sub>2</sub> partitioning between snow and air at equilibrium and 2) diffusion rates for H<sub>2</sub>O<sub>2</sub> in ice.

### Atmospheric Photochemical Modeling

South Pole is an ideal place to undertake atmospheric photochemical modeling because 1) the very cold temperatures and continental climate mean that homogeneous phase reactions dominate the photochemistry, making the modeling tractable, 2) the local area is relatively free of anthropogenic influence, and 3) a long time series of high quality, year round chemical, radiation, and meteorological measurements are available. These include surface ozone (O<sub>3</sub>), ozone burden and direct ultraviolet

radiation, air temperature, wind speed and direction, methane ( $\text{CH}_4$ ) and, more recently, carbon monoxide (CO) [Hofmann *et al.*, 1996]. The primary drawback to working at South Pole is that many model parameters, including chemical reaction and diffusion rates, must be extrapolated to the very cold temperatures that occur there.

As in our previous study at South Pole, we used steady-state photochemical model predictions at a number of discrete times during the sunlit time of year to define a representative annual cycle in atmospheric  $\text{H}_2\text{O}_2$ . The box model was designed specifically to model oxidants such as  $\text{H}_2\text{O}_2$  in polar conditions and uses a subset of the chemical reactions described in Stewart [1995] and Stewart and Thompson [1996]. Multi-year averages of air temperature, pressure, relative humidity, total ozone burden, carbon monoxide and surface ozone were used to parameterize the model. To our knowledge, the atmospheric concentration of  $\text{NO}_x$  at South Pole has not been measured so this was set at 1 pptv. Measurements of  $\text{NO}_x$  on the order of 1 to 2 pptv at Cape Grim support such an estimate for the pristine, Southern Hemisphere atmosphere [I. Galbally, *personal communication*]. Short term atmospheric measurements of  $\text{H}_2\text{O}_2$  (Figure 3) from November/December, 1994 are in agreement with model estimates while those from January, 1996 are somewhat lower, possibly because of local pollution from nearby construction.

### **Snow Pack Ventilation Modeling**

Air is driven through snow and firn as a result of pressure gradients. This process, called windpumping, is driven by barometric pressure variations, wind turbulence, and wind flow across the irregular snow surface [Waddington *et al.*, 1996]. The primary factors that control the level of windpumping are the magnitude of the surface forcing pressure and the permeability of the firn with depth. The former depends on a combination of the wind speed and the sastrugi geometry and the latter on grain size, sintering, and density in the firn. Using a ventilation model

described by *Albert* [1995] and permeability estimates based on grain sizes and density relationships, we predicted vertical ventilation vectors for snow pack permeability and surface forcing pressure scenarios. Grain size and density measurements included our own as well as those of others [*Giovinetto*, 1960; *Gow*, 1965].

Layers of dense, fine-grained, wind-packed snow have a marked effect on both ventilation rate and depth of penetration. Snow pits that we collected in late November, 1994 showed a 0.3 m layer at the surface of very fine-grained, dense snow with distinct syn-depositional features such as cross-bedding throughout. We interpreted this to be accumulation from the most recent winter. Conversely, snow pits collected in mid-January, 1996, showed no such features even though chemical analyses and accumulation records show clearly that accumulation from the most recent winter was preserved in the pits. In agreement with other work [*Harder et al.*, 1996], we believe that winter snow is originally fine-grained and densely packed by wind-redistribution. During the summer warming, however, the pack metamorphoses with larger grains growing at the expense of smaller grains [*Arons and Colbeck.*, 1995]. The syn-depositional features are mostly obliterated and the density (and so permeability) increases significantly. The result is that the winter layer (if it accumulates and persists) acts as a cap, restricting ventilation in winter and spring. Once this cap has matured and until a new cap forms, ventilation in late summer to early fall is enhanced.

The results of ventilation modeling are shown in Figure 4. The wind-packed, low permeability surface layer was assumed to exist in winter and spring and then metamorphose and disappear in summer. "High" winds (dotted) develop a surface forcing pressure of 2.5 Pa while "low" winds (dot-dash) develop 0.25 Pa. Winter (no symbol) sastrugi have a shorter spacing than in summer, so winter ventilation is vigorous near the surface but decays rapidly with depth. Assuming the same sastrugi wavelength as in summer but with the wind packed surface layer persisting, spring ventilation (filled circles) is reduced at the surface but penetrates deeper than

in winter. Summer ventilation (open diamonds) penetrates to large depths and is more vigorous at the surface than spring ventilation since the surface wind pack has matured. The small peak in ventilation at about 20 cm depth on all profiles results from a marked drop in density (and so increase in permeability) that corresponds to the previous year's summer/fall hoar layer. Note that mean annual wind speeds at South Pole are about  $5 \text{ m s}^{-1}$ , equivalent to the "low" wind condition or 0.25 Pa surface forcing pressure.

Because of the very wide variability in ventilation rates for different conditions, many of which are difficult to measure or quantify, an intermediate, low wind vertical ventilation rate with depth was used year round (solid). Ventilation was approximated using an exponential function with a maximum at the surface of  $0.00013 \text{ m sec}^{-1}$  and an e-folding depth of 1.0 m. These ventilation rates are in approximate agreement with those reported by *Cunningham and Waddington* [1993].

### Snow Pack Temperature Modeling

Measured air temperature, relative humidity, and wind speed were used in the snow pack temperature model SNTHERM [*Jordan*, 1991] to estimate snow pack temperatures with depth for the duration of the transfer modeling and snow pack simulation. Snow pack temperature at any time and depth during the snow pack simulations was interpolated from this 2-D temperature field (Figure 5).

### Chemical Transfer and Snow Pack Model

The amount of  $\text{H}_2\text{O}_2$  incorporated into precipitation is strongly temperature dependent and, we assume, determined by co-deposition of water and  $\text{H}_2\text{O}_2$  in proportion to their gas phase concentrations [*Neftel et al.*, 1995]. *Conklin et al.* [1993] and later *Winterle* [1996] used column experiments in the laboratory to estimate equilibrium partitioning between snow and air. Particularly at the very cold temperatures found in polar regions, such measurements are difficult to make

because they must be of very long duration. In this study, we used the equilibrium relationship,  $K_D$ , determined in our earlier study at South Pole [McConnell *et al.*, 1997c] which is somewhat higher than that published by Conklin *et al.* [1993] (Figure 6). As indicated by laboratory measurements, Winterle [1996] also concluded that the Conklin *et al.* [1993] line was low.

Because concentrations from co-deposition are super-saturated with respect to the solid phase, snow releases  $H_2O_2$  after formation [Bales *et al.*, 1995]. The time required to reach equilibrium is long and surface conditions like temperature and atmospheric concentration of  $H_2O_2$  change relatively quickly. The result is an equilibrium concentration target that is very likely changing faster than the snow's capacity to adapt, so the surface snow concentration is essentially always in some state of disequilibrium.

In this snow pack model and in our earlier work at South Pole, we assumed that  $H_2O_2$  is contained in the bulk ice and not adsorbed on the surface. Consequently, uptake and release are controlled by diffusion into and out of the snow grains, depending on the distribution of  $H_2O_2$  in the grain, the temperature, the grain shape and size, and the concentration of  $H_2O_2$  in the air at the outside boundary of the grain. We assumed that snow is made up of radially symmetric, spherical grains with radius,  $r$ , and used a finite-difference approximation of the spherical diffusion equation to model uptake and release of  $H_2O_2$  resulting from changing firm air concentrations. Each grain was typically approximated with 10 concentric shells. The spherical diffusion equation is:

$$\frac{\partial C_r}{\partial t} = \frac{D_i}{r^2} \frac{\partial}{\partial r} \left[ r^2 \frac{\partial C_r}{\partial r} \right] \quad (1)$$

where  $C_r$  is the local  $H_2O_2$  concentration at any point in the ice sphere and  $D_i$  is the diffusion coefficient in ice. Based on laboratory measurements at -5, -30, and -50 °C [Winterle, 1996],  $D_i$  is highly temperature-dependent and can vary as much as 2 orders of magnitude during the year at South Pole. As with snow-air equilibrium

partitioning, we extrapolated these measured values to snow pack temperatures using the van't Hoff equation. At  $-15^{\circ}\text{C}$ , the diffusion rate for  $\text{H}_2\text{O}_2$  is  $2.3 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$  which compares to  $10^{-16} \text{ m}^2 \text{ s}^{-1}$  for hydrochloric acid (HCl) and  $10^{-14} \text{ m}^2 \text{ s}^{-1}$  for nitric acid ( $\text{HNO}_3$ ) at this temperature [Domine and Thibert, 1995].

Snow is eventually buried and cut off from contact with the atmosphere and so preserved in some state of disequilibrium, depending on how long it has remained at the surface after original precipitation, how quickly the snow can release or take up  $\text{H}_2\text{O}_2$ , how quickly surface conditions are changing and how quickly the snow is buried. We view the snow pack as a diffusive medium with air containing  $\text{H}_2\text{O}_2$  circulating through it. Movement of  $\text{H}_2\text{O}_2$  is described using a finite-difference approximation to the 1-D advection-dispersion equation:

$$\frac{\partial C_{air}}{\partial t} = D \frac{\partial^2 C_{air}}{\partial z^2} - U \frac{\partial C_{air}}{\partial z} + SS \quad (2)$$

where  $C_{air}$  is the concentration of  $\text{H}_2\text{O}_2$  in the circulating air,  $t$  and  $z$  are time and depth respectively,  $D$  is the dispersion,  $U$  is the velocity of the air in the  $z$  direction, and  $SS$  represents the sources and sinks for  $\text{H}_2\text{O}_2$  within the snow pack [Bales and Choi, 1996]. For continuity to hold,  $U$  must average to zero over time. The dispersion term,  $D$ , includes both molecular diffusion and mechanical dispersion although mechanical dispersion is several orders of magnitude greater than molecular diffusion at depths less than several tens of meters. In the model, the mechanical dispersion term is proportional to the level of turbulent ventilation and the density. For completeness, we have included a temperature and density-dependent approximation to molecular diffusion following Whillans and Grootes [1985]. As discussed above, the source and sink term,  $SS$ , is determined by the rate of diffusion into and out of modeled snow grains.

### Snow Pack Model Summary

During snow pack simulation, snow accumulates on the surface and forms a layer of specified thickness and density. All accumulation is modeled as newly precipitated



snow and not wind drift. It is assumed that grain-scale diffusion can be characterized by a representative or effective grain radius. For South Pole simulations, we took  $80 \times 10^{-6}$  m as the effective grain radius throughout the year, following *Harder et al.* [1996]. Initial density at the surface was assumed to be  $0.35 \text{ g cm}^{-2}$  and constant throughout the year. Timing of layer accumulation is determined by a specified accumulation history for the site. At the time of layer accumulation,  $\text{H}_2\text{O}_2$  is modeled as uniformly distributed within the grain and concentration determined by co-deposition and measured air temperature ( $\sim 10\text{m}$ ). Snow can release and/or take up  $\text{H}_2\text{O}_2$  from the surrounding air as conditions change and as the snow moves from co-deposition concentrations toward equilibrium, although in the model, grain radius does not change after formation. The circulating air, or firn air, concentration  $C_{air}$  of  $\text{H}_2\text{O}_2$  is calculated by solution of the finite-difference approximation of the advection-dispersion equation (2). Snow pack temperature and ventilation is interpolated from the 2-D fields that result from separate modeling. The atmospheric  $\text{H}_2\text{O}_2$  concentration at the upper boundary is interpolated from a time series resulting from separate photochemical modeling. At the lower boundary, the change in firn air concentration near the bottom of the snow pack is projected across the boundary and the result assigned to the firn air at the bottom of the modeled snow pack. In order to minimize edge effects, the bottom of the simulated snow pack is padded with snow layers that have concentrations varying with depth that are consistent with the start date of the simulation.

As burial ensues, contact with the air at the top of the snow pack is progressively reduced. Densification occurs and, for South Pole, is described using an empirical depth-density relationship [*Mosley-Thompson et al.*, 1995]:

$$\rho = -4.8 \times 10^{-4} Z^2 + 0.0196 Z + 0.35 \quad (3)$$

where  $\rho$  is layer density in  $\text{g cm}^{-3}$  and  $Z$  is depth in meters. Note that if deflation occurs, the appropriate number of whole or fractional layers is stripped from the

model and layer depth adjusted accordingly. Density is not reduced when layers are brought closer to the surface.

The firn air concentration,  $C_{air}$ , was computed in these simulations with a time step on the order of 30 minutes (Equation 2), while spherical grain diffusion was computed with a 6 minute time step (Equation 1). Tests indicated that there was little sensitivity in the model results to time steps in these ranges.

## Results

### Surface Snow Simulations

The results of more than two years of year round weekly surface snow sampling are shown in Figure 7.  $H_2O_2$  values range from the mid-winter concentrations of 2-3  $\mu M$  to more than 20  $\mu M$  in spring. Note the repeatability in the annual cycle in surface snow concentration, although the spring peak is somewhat lower in 1996 than in 1995. The snow sample water equivalent depths averaged 0.055 g cm<sup>-2</sup> and mean depths were approximately consistent from sample period to sample period. Variability in individual sampling depth within each sampling period was quite large, however.

For comparison with our earlier transfer modeling work at South Pole [McConnell *et al.*, 1997c], the snow pack model was used to simulate the expected surface snow concentrations of  $H_2O_2$  in very near-surface snow from Jan, 1994 through July, 1997. Surface snow physical parameters, including representative grain radius and ventilation, were different from those used in the deeper pit simulations. Three representative grain radii were tested: 20, 40 and 80  $\mu m$  (Figure 8). Note that Harder *et al.* [1996] report blowing snow radii at South Pole from 15  $\mu m$  in winter to 30  $\mu m$  in summer. Ventilation in the very shallowest snow pack was assumed to be very rapid, meaning that the top 0.0015 m of snow was in unrestricted contact with the atmosphere above. This was accomplished by setting both the lower and upper boundary conditions in a 10 layer, 0.015 m snow pack to the modeled atmospheric

concentration. While the annual atmospheric concentration cycle was kept constant from year to year, measured air temperatures were used to model snow pack and skin temperatures, leading to some year to year variability in simulated surface snow concentration.

### Snow Pit Simulations

Figure 9 shows the simulated snow pit concentration for the given monthly accumulation histories (Figure 2) along with measured  $\text{H}_2\text{O}_2$  concentration. Note that these simulations included a constant annual cycle in atmospheric concentration. Because there can be large differences in depositional temperature and atmospheric concentration across a month, we linearly interpolated the accumulation records to an approximate 1 cm nominal layer thickness and then determined the deposition time for that 1 cm layer (Figure 2). The formation temperature for each layer, estimated from the measured  $\delta^{18}\text{O}$  profile for each pit, is plotted along with the simulation formation temperature (Figure 10). Note that the formation temperature was estimated from measured  $\delta^{18}\text{O}$  using a linear relationship with slope 2.3 o/oo ( $^{\circ}\text{C}^{-1}$ ) (after *Jouzel and Merlivat* [1984]) and the intercept adjusted to give the desired mean. This estimated formation temperature was back-diffused using a high-boost filter and layer-stripping algorithm (after *Sigg et al.* [1994]).

Additional snow pack simulations were made using mean monthly accumulation rates observed at South Pole [*McConnell et al.*, 1997b]. Accumulation rate and timing, atmospheric concentration, and temperature were repeated from year-to-year. Annual accumulation was approximated with 24 layers, each with a nominal thickness of 0.0121 m (Figure 11). For comparison, the running yearly average from the mean monthly accumulation simulation is plotted with the 4 observed  $\text{H}_2\text{O}_2$  profiles. In general, the simulation under predicts the observed pit concentrations, although much of the discrepancy may be because accumulation for these 4 pits is not well represented by the mean monthly values used in the simulation.

## Discussion

### Surface Snow Simulations

In our earlier transfer modeling work at South Pole [McConnell *et al.*, 1997c], surface snow concentrations of  $\text{H}_2\text{O}_2$  were inverted, using a snow grain diffusion model, to an estimate of the atmospheric concentration. However, the previous snow grain model used an analytical solution to the spherical diffusion equation (Equation 1) that assumed a uniform concentration at the start of each weekly time step. To assess the impact of that approximation, the finite-difference, grain-diffusion model was used to simulate expected surface snow concentrations for the given model atmospheric concentration. If the approximation in the earlier model is not significant, then the simulated and observed surface snow concentration profiles should approximately match.

As shown in Figure 8, the new model does not replicate the observed surface snow time series with the grain radius used in the earlier study. In particular, the rapid spring rise in concentration in 1995 cannot be matched unless a smaller grain radius of  $40\ \mu\text{m}$  is used. While this grain radius is well within the expected range for surface snow, release of  $\text{H}_2\text{O}_2$  in the late summer and autumn is too rapid, resulting in snow concentrations lower than observed at that time.

To understand the differences between the previous and present grain diffusion models, the distribution of  $\text{H}_2\text{O}_2$  within the grains is shown in Figure 12 for the  $80$  and  $40\ \mu\text{m}$  grains. With a radius of  $80\ \mu\text{m}$ , there is approximately a 5 week lag in response between the center and outside of the grain. This lag provides “memory” for larger grains that is reduced or missing in smaller grains. Distribution of  $\text{H}_2\text{O}_2$  within the grain is most uniform during mid-summer when the snow is warmest and the diffusion rate at a maximum. Therefore, the very sharp peak in early November, when temperatures are low, can be replicated only with very small grains on the order of  $40\ \mu\text{m}$  because the center of the larger grain remains essentially unchanged for some time. However, the subsequent release of  $\text{H}_2\text{O}_2$  after the surface has warmed

in mid-summer and fall is too rapid in the smaller grain. In sum, the distribution of  $\text{H}_2\text{O}_2$  in the grain is clearly not uniform during most of the annual cycle, making the assumption of uniformity in the earlier study invalid.

It should be stressed that these surface snow simulations assume that the surface snow is entirely comprised of "old" snow. That is, snow that precipitated sometime previously and has been in contact with the atmosphere during that time. If samples at the time of the sharp spring rise in surface snow  $\text{H}_2\text{O}_2$  included newly precipitated snow, then the model simulation will require smaller grains radii than actual to compensate. Because the diffusion rate increases exponentially with temperature, then newly precipitated snow during periods of cold snow temperatures will have a more significant impact on simulations than new precipitation during warm periods. This suggests that this technique of inverting surface snow samples to an estimate of the atmospheric concentration is more robust in summer than winter.

### **Snow Pit Simulations**

In general, agreement and disagreement between simulated and observed values occurs simultaneously in the  $\text{H}_2\text{O}_2$  concentration (Figure 9) and the formation temperature (Figure 10) profiles (pit 6, 0.2 to 0.6 m). This suggests that at these depths, either the monthly accumulation record is incorrect, the depth-density map is in error, or accumulation at these times was a result of drifting snow and not new precipitation. As expected, agreement is better between simulated and observed profiles for estimated formation temperature than for  $\text{H}_2\text{O}_2$  because the relation between formation temperature and  $\delta^{18}\text{O}$  is linear and because air temperatures were measured for the entire duration of snow pit accumulation. However, this agreement between simulated and observed formation temperature indicates that the accumulation histories are generally accurate and that the depth-density relationship used in the snow pack model is approximately correct.

The character of many features, such as the sharp, 7 cm low concentration layer

in pit 10 at 35 cm depth followed by the distinct maximum at 44 cm, are replicated in the simulations for  $\text{H}_2\text{O}_2$ , although sometimes with a shift in depth. This replication of the observed variability indicates that the model captures most of the physical processes in atmosphere-to-snow-to-firn transfer at South Pole. The occasional shifts in depth between observed and simulated profiles is not surprising for a number of reasons. First, accumulation was recorded only once a month and so we linearly interpolated the monthly accumulation record to a smaller time interval. However, there may be up to 1 month difference between the model accumulation date and that when accumulation actually occurred since a month's accumulation may have occurred the day before or after a measurement was taken. Second, the accumulation stakes were reset either once or twice a year (to accommodate rising snow level) which may have introduced error of unknown magnitude into the accumulation histories. Third, even if the accumulation histories are exactly correct, uneven compression of the snow layers during firnification will lead to a non-linear and perhaps sporadic mismatch between model and observed snow pits since densification in the model is assumed to follow the smooth depth-density relation given by Equation 3.

In general, winter minima in the simulations were below those observed for both  $\text{H}_2\text{O}_2$  and formation temperature. For  $\text{H}_2\text{O}_2$ , these winter-time concentrations change very little from their original deposition concentration since temperatures are very cold and diffusion very slow when this snow is at or near the surface. The likely explanation for the lower-than-observed winter minima is that the model paradigm – accumulation only resulting from new precipitation and not drifting of existing snow – does not hold for much of the winter. In contradiction to this, *Gow* [1965] concluded that accumulation mostly occurred in winter. Additional explanations would be that concentration at the time of formation is not determined by co-deposition or that winter snow grains are much smaller than summer grains, leading to enhanced uptake of  $\text{H}_2\text{O}_2$  by diffusion well after deposition. Uptake could also occur during recrystallization of the pack during summer warming but such snow metamorphism

and grain growth is beyond the scope of this modeling study.

Snow pit simulations using mean monthly accumulation rates (Figure 11) indicate that firn continues to lose  $\text{H}_2\text{O}_2$  to the atmosphere for about 8-10 years after precipitation, or about 2.5-3.0 m depth for current South Pole conditions. Below this depth, there is apparently little additional loss but the amplitude of the annual cycle continues to decrease because of vapor phase diffusion. This loss to the atmosphere is related to the ventilation rate, snow grain radius, snow pack temperature throughout the year, and to the accumulation rate since rapid burial will cut off exchange with the atmosphere more quickly. A comparison of simulated mean annual concentration of  $\text{H}_2\text{O}_2$  after 10 years with different annual accumulation rates (Figure 13) demonstrates that there is a marked, approximately linear increase in preserved  $\text{H}_2\text{O}_2$  with increasing accumulation rate. That is, increases in annual accumulation rate will result in increases in  $\text{H}_2\text{O}_2$  in firn and ice cores. Note that *Jouzel et al.* [1983] reported recent increases in accumulation at South Pole as measured in firn cores which is in agreement with long term, spatial accumulation studies by *Mosely-Thompson et al.* [1995]. This recent increase in accumulation rate should translate to an increase in firn core concentrations of  $\text{H}_2\text{O}_2$  near the surface.

## Conclusions

The physically based advection-dispersion and snow grain diffusion model presented here provides insight into the deposition, subsequent uptake and release, and final preservation of  $\text{H}_2\text{O}_2$  in the snow and firn. While longer duration and winter atmospheric measurements of  $\text{H}_2\text{O}_2$  would reduce uncertainty considerably, the results of the modeling indicate that the surface snow is essentially always out of equilibrium since environmental conditions like temperature and atmospheric concentration are changing faster than the snow's capacity to adapt. Even very near-surface snow concentrations, while strongly reflecting the atmospheric concentration, do not have sufficient time, especially at winter temperatures, to come to equilibrium with the

atmosphere. When cut off from vigorous exchange with the atmosphere, the firn air quickly establishes equilibrium with the outside of the snow grains. Results also suggest that accumulation in winter at South Pole often does not only consist of newly precipitated snow but has some component of drifted older snow.

As in our earlier snow pit modeling at Summit, Greenland, the large variability in the concentration profiles among 4 snow pits at South Pole leaves no doubt about the importance of accumulation seasonality in determining the final  $\text{H}_2\text{O}_2$  and  $\delta^{18}\text{O}$  preserved in firn and ice. This supports the need for using multiple cores and pits to investigate short-term atmospheric phenomena. The character of many of the features unique to each pit were successfully replicated in model simulations of both  $\text{H}_2\text{O}_2$  and formation temperature, and this, with only monthly accumulation histories. Ultimately, accumulation timing and formation temperature must come from the chemical record itself via modeling of more than one chemical species simultaneously. This will require detailed knowledge of transfer functions for seasonally dependent species other than  $\text{H}_2\text{O}_2$  and  $\delta^{18}\text{O}$  and incorporation of this understanding into physically based numerical models.

Long duration snow pit simulations using mean monthly accumulation rates measured at South Pole indicate that the firn continues to lose  $\text{H}_2\text{O}_2$  to the atmosphere for at least 8-10 years, depending on grain size, temperature, and accumulation and ventilation rates. However,  $\text{H}_2\text{O}_2$  analyses on a number of shallow firn cores from South Pole with co-registered  $\delta^{18}\text{O}$  and physical measurements like grain size, are needed to verify this result. The apparent dependence of preserved mean annual  $\text{H}_2\text{O}_2$  simply on such parameters as annual accumulation rate, emphasizes the importance of using physically based numerical models to quantitatively interpret observed snow pit and ice core records.

**Acknowledgments.** This work was supported by a NASA Graduate Fellowship for Global Change and in part by National Science Foundation's Office of Polar Program.



Atmospheric photochemical modeling at NASA was supported by the Goddard Director's Discretionary Fund. Field work at South Pole was conducted under a cooperative agreement with the NOAA Climate Monitoring and Diagnostics Laboratory. We very much appreciate the efforts of K. McNitt, M. Boland, J. Otten, B. Halter and T. Swanson of NOAA/CMDL for their help at South Pole and S. Oltmans and P. Novelli for access to the surface ozone and carbon monoxide data respectively. We also thank A. Long and D. Dettman for access to the University of Arizona stable isotope lab and B. Snider for her help with laboratory measurements.

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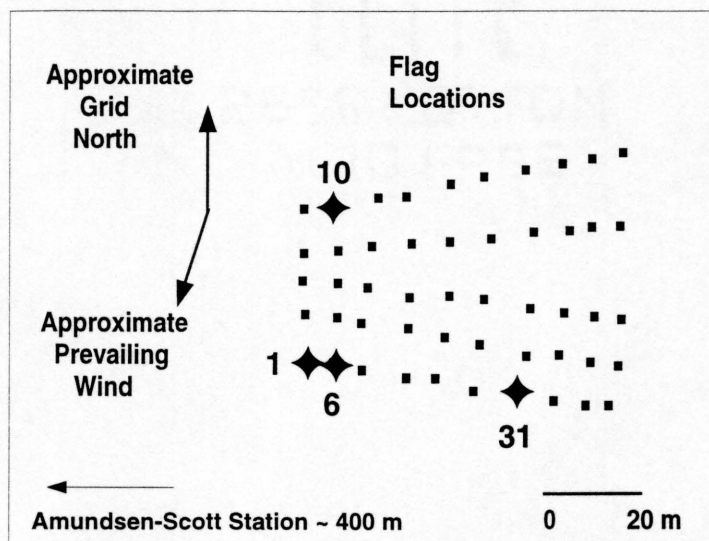
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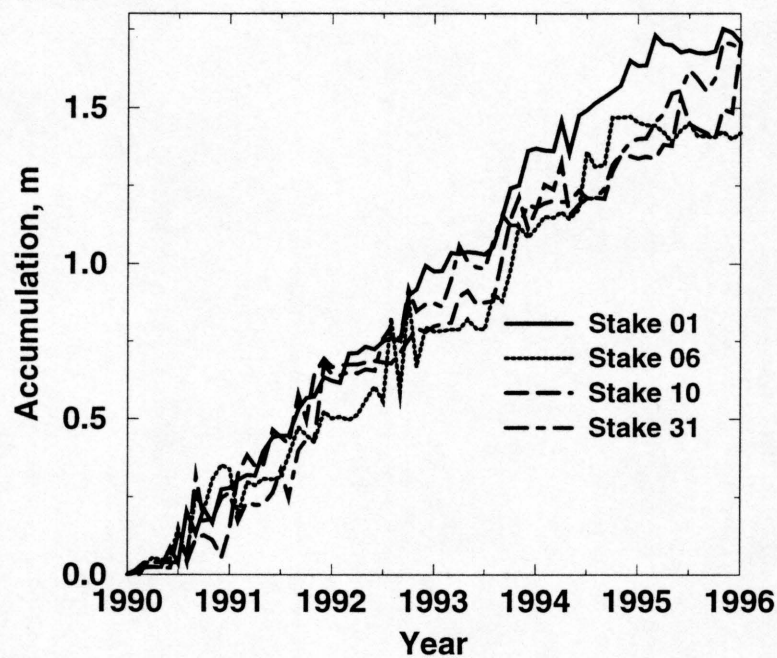
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**Figure 1.** Map of the long-term, snow stake accumulation field with locations of snow pits indicated.



**Figure 2.** Time-depth map for the four snow pits sampled at South Pole in January, 1996

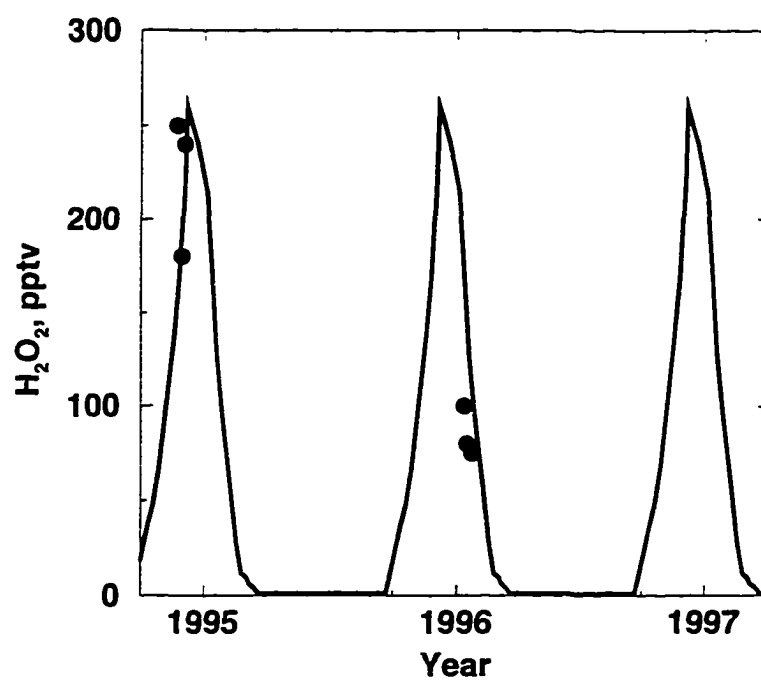
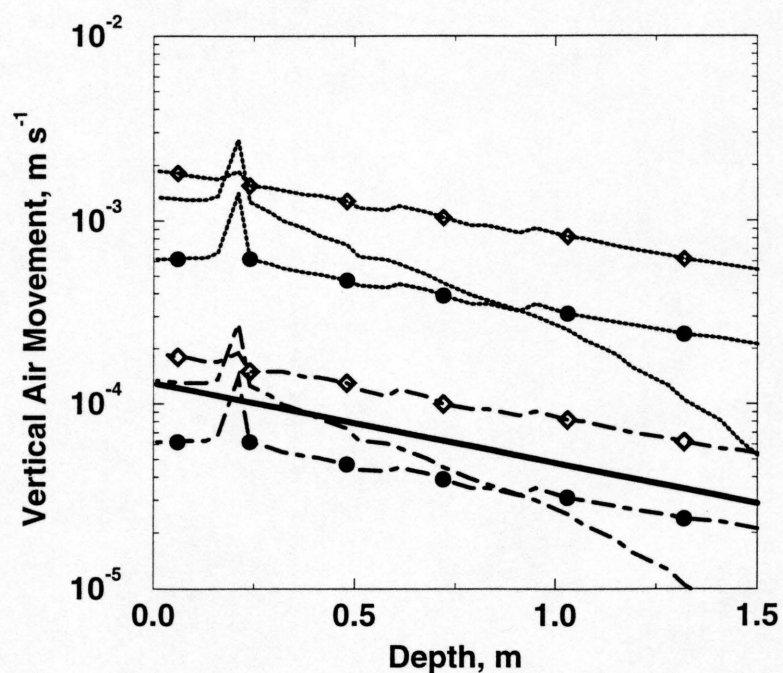
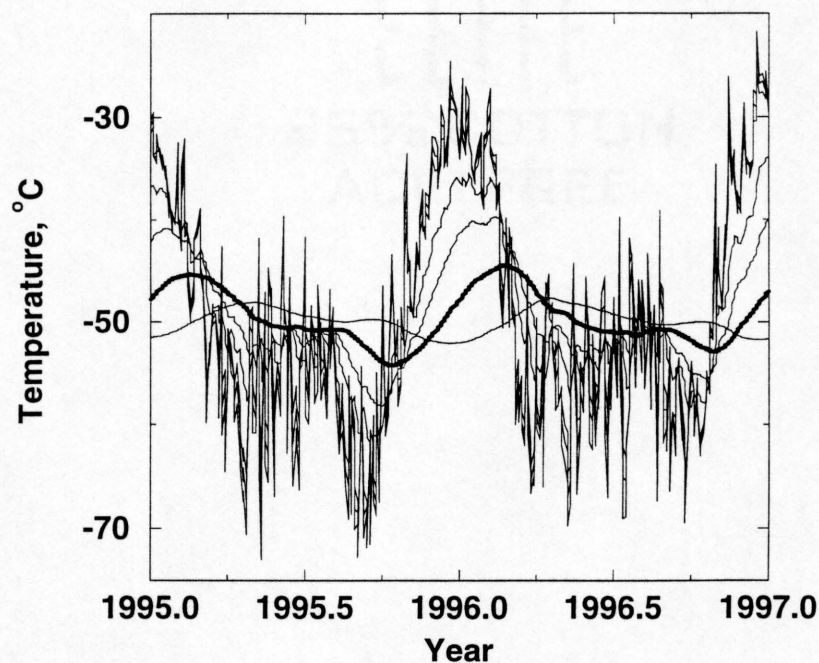


Figure 3. Spot measurement (circles) of atmospheric H<sub>2</sub>O<sub>2</sub> at South Pole and the repeated annual cycle used in surface snow and snow pack simulations. The latter was estimated using a photochemical box model [McConnell *et al.*, 1997c].

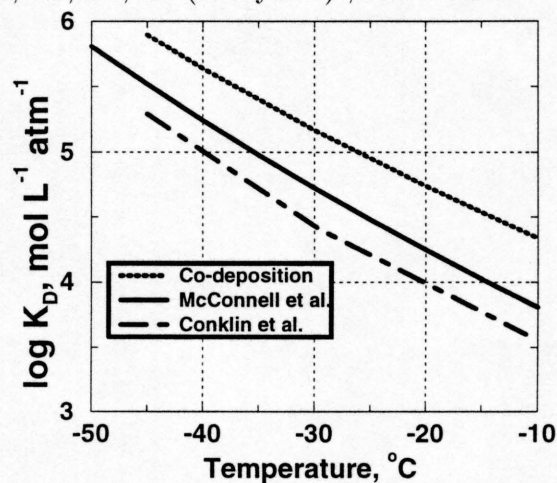


**Figure 4.** Modeled snow pack ventilation at South Pole. High wind conditions (dotted) assumed a surface forcing pressure of 2.5 Pa and low wind 0.25 Pa (dash-dot). Winter (no symbol) and spring (filled circles) snow packs included a high density, fine-grained wind pack layer at the surface. Summer (diamonds) snow packs did not include this layer. The ventilation rate with depth used in snow pack simulations is indicated (solid).





**Figure 5.** SNTHERM model snow pack temperatures used in the snow pack simulations at 0.01, 0.10, 0.5, 1.0, 2.0 (heavy line) , and 4.0 m.



**Figure 6.** Snow-atmosphere partitioning relations determined by laboratory experiments [Conklin *et al.*, 1993] and previous transfer modeling at South Pole [McConnell *et al.*, 1997c]. Co-deposition refers to equal rate of condensation of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$ , resulting in the same molar ratio in frozen particles as in the air.

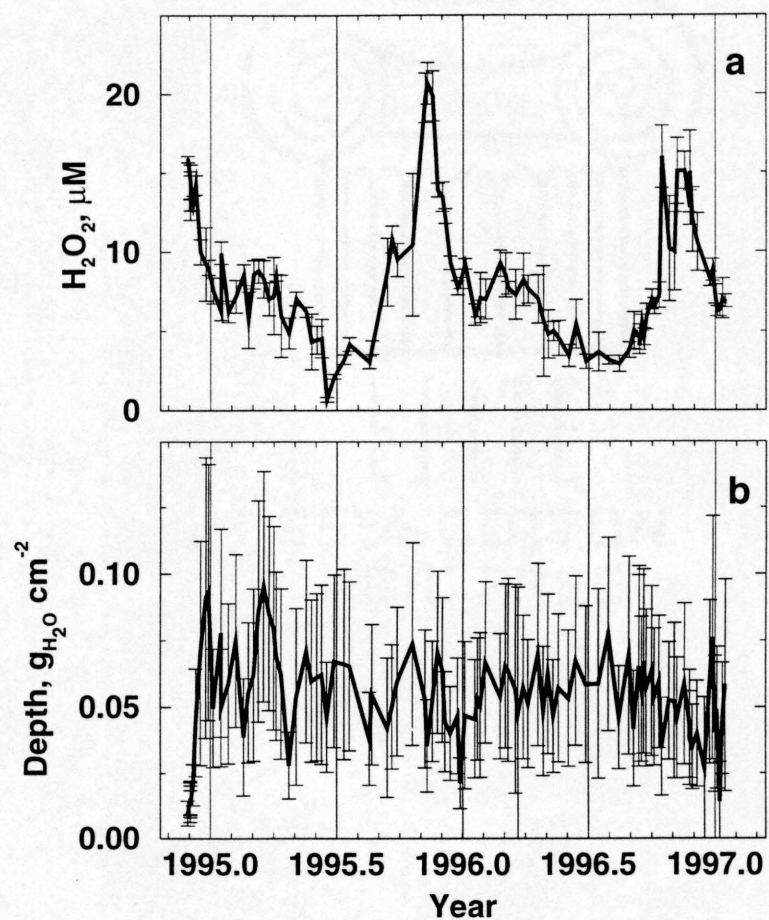
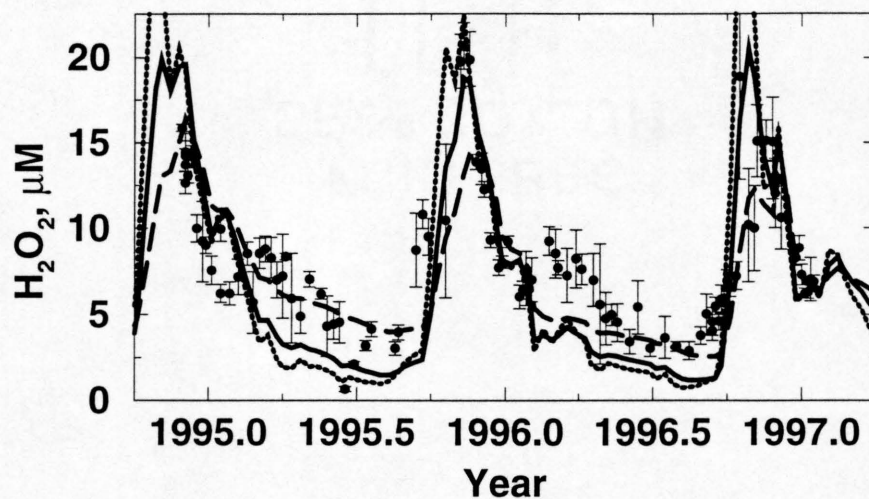
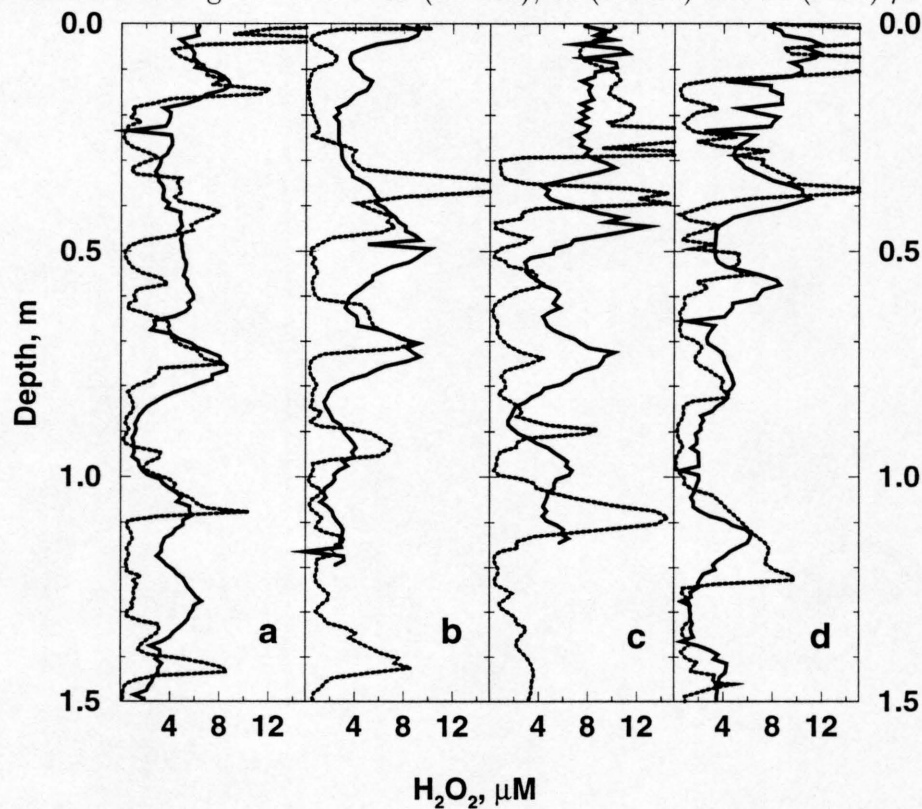


Figure 7.  $\text{H}_2\text{O}_2$  concentrations (a) and sample depth (b) in surface snow at South Pole. Error bars show 1 standard deviation.

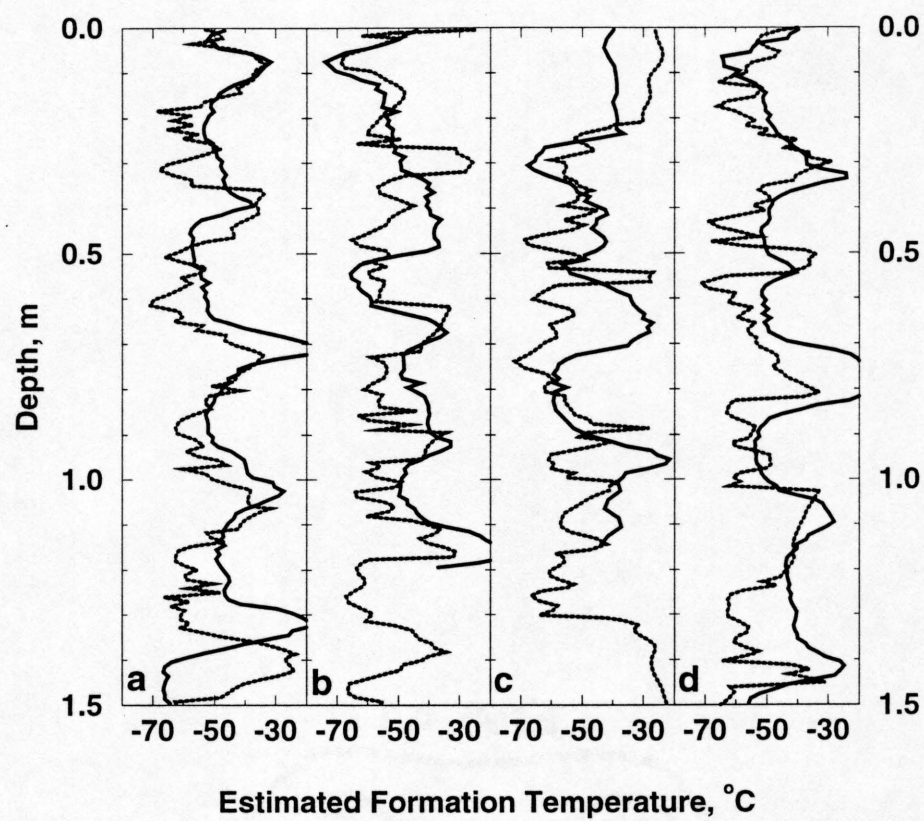


**Figure 8.** Observed (circles) and simulated surface snow concentrations at South Pole for effective snow grain radii of 80 (dashed), 40 (dotted) and 20 (solid)  $\mu\text{m}$ .

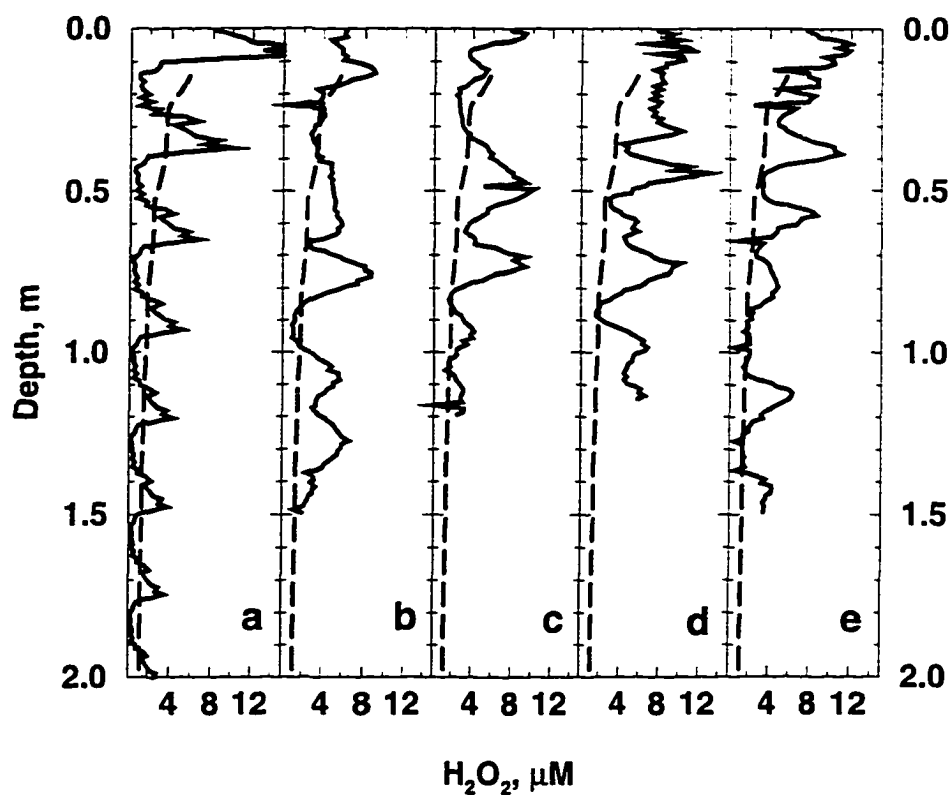


**Figure 9.** Measured (solid) and simulated (dashed) concentration profiles for 4 snow pits at South Pole. The pits were sampled in January, 1996.





**Figure 10.** Measured (solid) and simulated (dashed) formation temperature profiles for the snow pits in Figure 9.



**Figure 11.** Snow pack simulation (a) using mean monthly accumulation at South Pole (following *McConnell et al.*, [1997b]). For comparison with observations, the running annual average for the pit simulation (a) is plotted with the observed profiles at stakes 01 (b), 06 (c), 10 (d), and 31 (e). Note that the simulation curve is generally lower than the observed profiles, indicating that the snow pack model may be under predicting the snow concentration with depth.

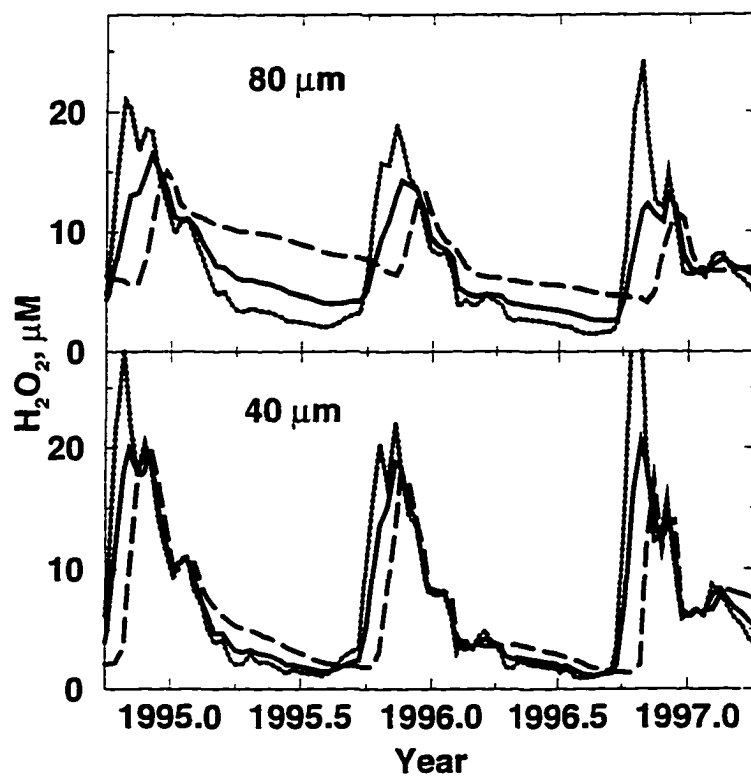
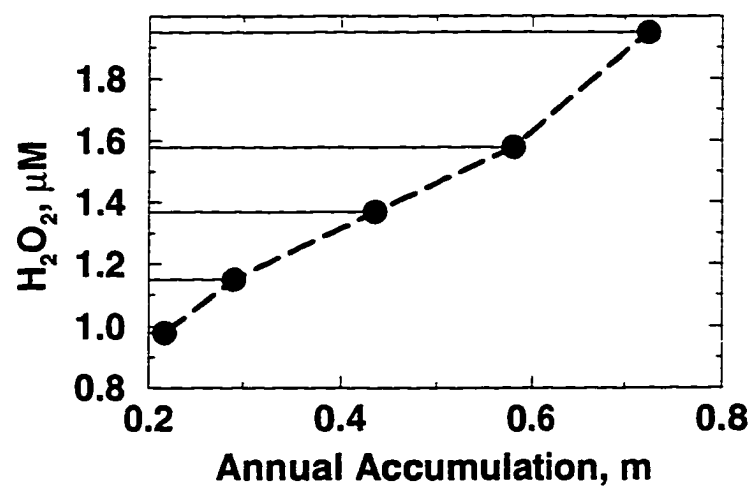


Figure 12. Distribution of  $\text{H}_2\text{O}_2$  in snow grains during simulations of surface snow concentrations. Response of the inner shell (dashed) lags the mean (solid) by approximately 5 weeks for an  $80\ \mu\text{m}$  grain radius while that of the outer shell (dotted) leads.



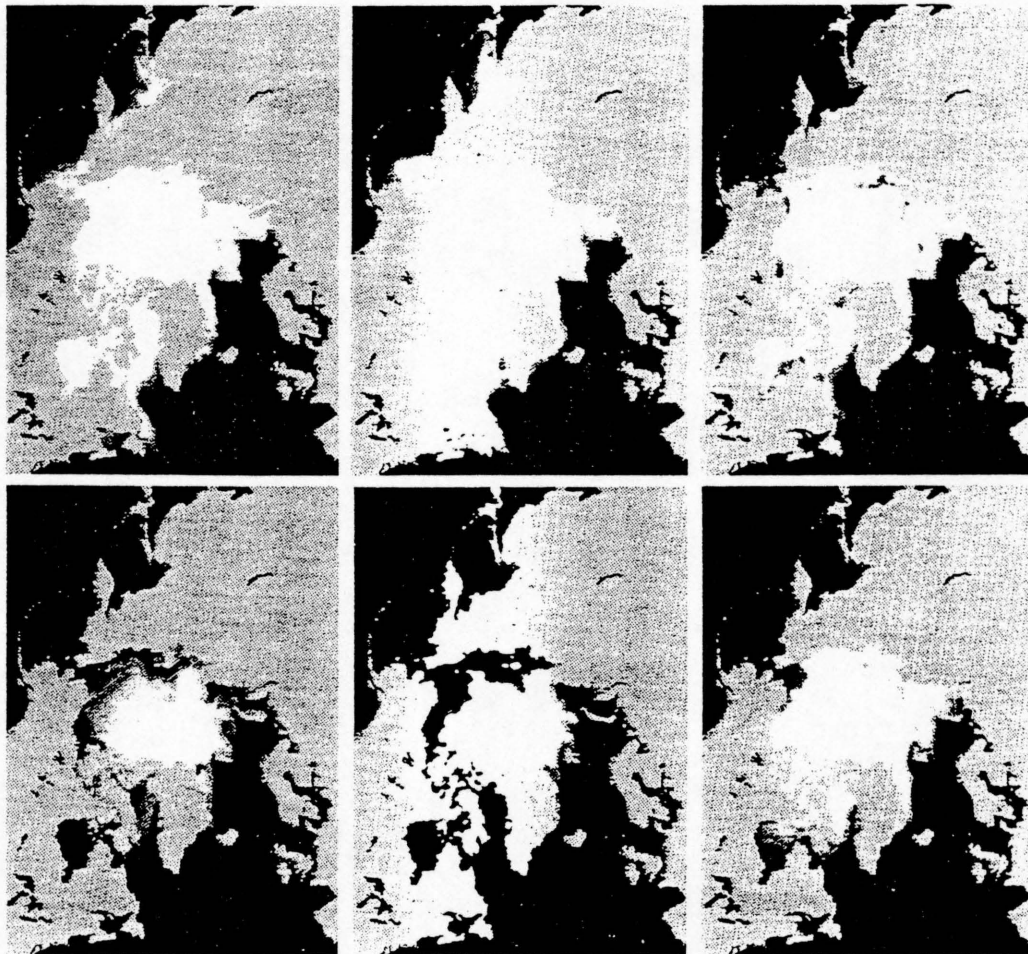
**Figure 13.** The dependence of annual average  $\text{H}_2\text{O}_2$  in simulated snow pits approximately 10 years after burial on annual accumulation rate. Current South Pole annual accumulation was modeled as 0.29 m.

## **Appendix C**

### **Physically Based Inversion of Surface Snow Concentrations of H<sub>2</sub>O<sub>2</sub> to Atmospheric Concentrations at South Pole**



# Geophysical Research Letters



FEBRUARY 15, 1997

Volume 24 Number 4

AMERICAN GEOPHYSICAL UNION



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## Physically based inversion of surface snow concentrations of $\text{H}_2\text{O}_2$ to atmospheric concentrations at South Pole

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**Abstract.** Inversion of chemical records archived in ice cores to atmospheric concentrations requires a detailed understanding of atmosphere-to-snow-to-ice transfer processes. A unique year-round series of surface snow samples, collected from November, 1994 through January, 1996 at South Pole and analyzed for  $\text{H}_2\text{O}_2$ , were used to test a physically based model for the atmosphere-to-snow component of the overall transfer function. A comparison of photochemical model estimates of atmospheric  $\text{H}_2\text{O}_2$ , which are in general agreement with the first measurements of atmospheric  $\text{H}_2\text{O}_2$  at South Pole, with the inverted atmospheric record (1) demonstrate that the surface snow acts as an excellent archive of atmospheric  $\text{H}_2\text{O}_2$  and (2) suggest that snow temperature is the dominant factor determining atmosphere-to-surface snow transfer at South Pole. The estimated annual cycle in atmospheric  $\text{H}_2\text{O}_2$  concentration is approximately symmetric about the summer solstice, with a peak value of  $\sim 280$  pptv and a minimum around the winter solstice of  $\sim 1$  pptv, although some asymmetry results from the springtime stratospheric ozone hole over Antarctica.

### Introduction

Ice cores provide a detailed record of past changes in atmospheric chemistry and meteorology. Chemical species are incorporated into snow and thence ice through wet and dry deposition. Most aerosols are irreversibly deposited, meaning they are not emitted back to the atmosphere after deposition. More-volatile species such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), formaldehyde, and organic acids are reversibly incorporated in the snow. Some fraction of the deposited mass of these species returns to the atmosphere as precipitation ages and as surface and near-surface conditions change.

Quantitative interpretation of an ice core record requires detailed knowledge of the transfer processes that relate local atmospheric concentrations of chemical species to those found in surface snow, firn, and ice [Nefel, 1996]. This is particularly important for reversibly deposited species since post-depositional processes may play a more important role in determining the ice-core concentration than do depositional fluxes.  $\text{H}_2\text{O}_2$ , which

shows strong post-deposition modification, is a good model for other reversibly deposited chemical species [Bales and Wolff, 1995]. A mathematical description of these transfer processes, referred to as the transfer function, can be formulated in the forward sense that describes how  $\text{H}_2\text{O}_2$  in air is incorporated into snow and firn. In an example of a forward model, McConnell *et al.* [1996b] developed an empirical, lumped-parameter model to simulate  $\text{H}_2\text{O}_2$  concentrations in a snow pit given photochemical modeled estimates of the atmospheric concentration of  $\text{H}_2\text{O}_2$  and a priori knowledge of the timing of snow accumulation from automatic depth gauges. Simulations were compared to observed profiles to define model parameters. The interpretation of the ice core record, however, requires inverse modeling, where ice core concentrations are inverted to an estimate of the atmospheric concentration. Non-linearities in the time-depth relationship and the convolution of those transfer processes active at the surface (e.g., partitioning between snow and air, post-depositional exchange with the atmosphere) with those active beneath the surface (e.g., diminished exchange during burial, redistribution of  $\text{H}_2\text{O}_2$  by vapor phase diffusion in the snow pack) hamper inversion of ice core records.

In this study, we estimated year-round atmospheric concentrations of  $\text{H}_2\text{O}_2$  at South Pole using a quantitative, physically based inversion of concentrations in snow samples. To test the inverse model, we used a unique, 14-month long series of surface snow samples, thereby avoiding both the non-linearities associated with the time-depth relationship in firn and the transfer processes active beneath the surface. We compared these inverted atmospheric concentrations with the first measurements of atmospheric  $\text{H}_2\text{O}_2$  at South Pole and with steady-state photochemical model predictions.

### Methods

Surface snow samples were collected by NOAA winter-over staff in the Clean Air Sector at South Pole on approximately a weekly basis from November, 1994 through January, 1996. To mitigate spatial variability, each sample consisted of six surface snow scrapes with an average water-equivalent depth of  $0.5 \text{ g cm}^{-2}$ . The surface scrapes were aliquoted individually at South Pole and analyzed for  $\text{H}_2\text{O}_2$  at our lab in Arizona. Continuous, short term measurements of atmospheric  $\text{H}_2\text{O}_2$  were made in November/December, 1994 and in Jan-

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uary, 1996 at South Pole using a gas-phase detector [Bales et al., 1995a].

## Model

The amount of H<sub>2</sub>O<sub>2</sub> incorporated into precipitation is thought to be strongly temperature dependent and determined by co-deposition of water and H<sub>2</sub>O<sub>2</sub> in proportion to their gas phase concentrations. Snow on the ground releases H<sub>2</sub>O<sub>2</sub> since concentrations from co-deposition are supersaturated with respect to the solid phase [Bales et al., 1995]. The ice-air equilibrium relation, also a strong function of temperature (Figure 1), was confirmed by objective optimization of a lumped parameter model of the transfer function for H<sub>2</sub>O<sub>2</sub> using snow-pit data in Greenland [McConnell et al., 1996b]. The time required to reach equilibrium in the solid phase is relatively long and surface conditions like temperature and atmospheric concentration of H<sub>2</sub>O<sub>2</sub> change quickly, so the equilibrium concentration target is likely to be changing faster than the snow's ability to adapt. The result is a surface snow concentration that is essentially always out of equilibrium. This snow is eventually buried and cut off from contact with the atmosphere and so preserved in some state of disequilibrium, depending on how long it has remained at the surface after original precipitation, how quickly the snow can release or take up H<sub>2</sub>O<sub>2</sub>, how quickly surface conditions are changing, how quickly the snow is buried and the level of ventilation. Note that recent high-resolution snow pit data from South Pole [McConnell et al., 1996a] do not show any consistent loss of H<sub>2</sub>O<sub>2</sub> after burial.

In laboratory experiments, the rate of H<sub>2</sub>O<sub>2</sub> degassing from firn was found to be adequately described by a spherical diffusion model of individual snow grains within the firn:

$$\frac{\partial C_r}{\partial t} = \frac{D_i}{r^2} \frac{\partial}{\partial r} \left[ r^2 \frac{\partial C_r}{\partial r} \right] \quad (1)$$

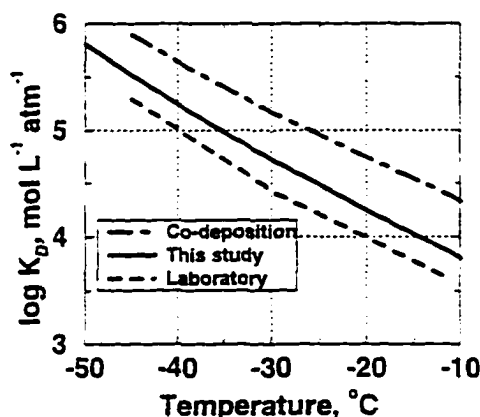


Figure 1. Snow-atmosphere partitioning relations determined by laboratory experiments [Conklin et al., 1993] and this study. Co-deposition refers to equal rate of condensation of H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>, resulting in the same molar ratio in frozen particles as in the air.

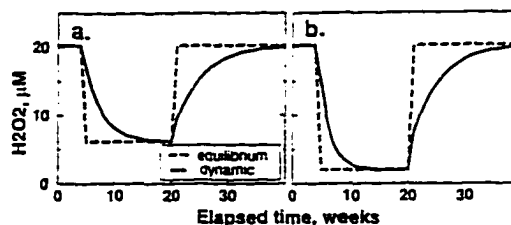


Figure 2. Simulated response of H<sub>2</sub>O<sub>2</sub> concentration in spherical ice grains (200 μm radius) to changes in temperature from a) -40 °C to -30 °C and b) -40 °C to -20 °C. Simulated temperatures increase at 4 weeks and return to -40 °C at 20 weeks. Gas-phase H<sub>2</sub>O<sub>2</sub> is 100 pptv.

where  $C_r$  is the local H<sub>2</sub>O<sub>2</sub> concentration at any point in the ice sphere and  $D_i$  is the diffusion coefficient in ice [Winterle, 1996]. We use this spherical diffusion model with a strongly temperature-dependent  $D_i$  (derived from independent laboratory experiments) to define a physically based snow response function to simulate how snow will uptake or release H<sub>2</sub>O<sub>2</sub> as environmental conditions change.

The simulated response of snow to changes in temperature is given in Figure 2. For a temperature increase from -40 to -30 °C (Figure 2a), it takes nearly 15 weeks for the initial 20 μM snow concentration to approach the new 6 μM equilibrium. When the temperature is changed back to -40 °C, equilibrium at the original concentration is achieved after 20 weeks. In the second simulation (Figure 2b), the temperature is raised from -40 to -20 °C. The new equilibrium concentration of 2 μM is approached after only about 6 weeks because of the higher diffusion coefficient at this warmer temperature.

Year-around, monthly accumulation data from South Pole suggest that an individual surface snow sample is predominately "old" snow [McConnell et al., 1996a], meaning that snow found at the surface precipitated some months prior to sampling and has been in contact with the atmosphere for that time. The histogram of the gross monthly accumulation recorded at fifty accumulation stakes for the period September, 1988 through January, 1996 shows a distinct mode around zero (Figure 3).

From the cumulative distribution function, the relative probability that the surface elevation has changed by less than 2.5 cm in a month is about 50%. If the surface elevation has changed, it is likely that the added accumulation is "old" surface snow that has been redistributed by wind. We make the simplifying assumption that surface snow samples are composed of "old" snow. Hence, post-depositional processes at the surface dominate precipitation processes and H<sub>2</sub>O<sub>2</sub> at South Pole is treated as a completely reversibly deposited chemical species.

We hypothesize that changes in surface snow concentrations are driven primarily by changes in surface temperature and atmospheric H<sub>2</sub>O<sub>2</sub>. Using the temperature-dependent spherical diffusion model and the computed skin temperature, the snow's response to changes in environmental conditions over the elapsed time between surface sampling is simulated to give  $R_f$ , the fraction of total equilibrium change in concentration

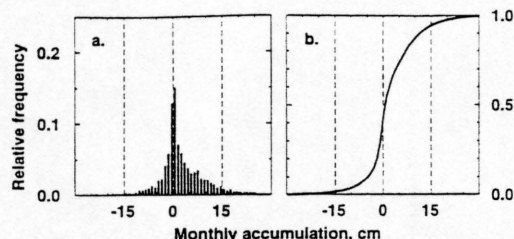


Figure 3. Histogram (a) and associated cumulative distribution function (b) of recent monthly snow accumulation at South Pole based on 50 stakes measured over a 7.5 year period [McConnell *et al.*, 1996a].

achieved after some elapsed time. In Figure 2,  $R_f$  starts at zero when the temperature is first changed from  $-40^\circ\text{C}$  to  $-30^\circ\text{C}$ , increases exponentially and approaches 1.0 after about 15 weeks. The equilibrium snow concentration is computed as:

$$S_{eq}(t) = \frac{S_{obs}(t-1) - S_{obs}(t)}{R_f} \quad (2)$$

where  $S_{eq}$  is the equilibrium concentration ( $\mu\text{M}$ ) of  $\text{H}_2\text{O}_2$  and  $S_{obs}$  is the observed concentration. With the temperature and the equilibrium snow concentration known, the atmospheric concentration is readily derived from the snow-atmosphere partitioning relationship ( $K_D$ ) (Figure 1).

## Results

Surface snow concentrations showed a pronounced, repeatable seasonal cycle with a maximum of ( $\sim 22 \mu\text{M}$ ) in early to mid-November, well before the summer solstice, and a broad minimum of ( $\sim 2 \mu\text{M}$ ) near the winter solstice (Figure 4). Spatial variability in surface concentration is generally far lower than temporal variability. Continuous atmospheric  $\text{H}_2\text{O}_2$  measurements, presented as weekly averages (Figure 5), were 200–250 pptv in Nov/Dec, 1994 and 90–100 pptv in Jan, 1996. No diel cycle in atmospheric concentration was seen.

### Atmospheric Photochemical Model Estimates

Steady-state photochemical model predictions at seven discrete times during the sunlit time of year were used to define a representative annual cycle in atmospheric  $\text{H}_2\text{O}_2$  (Figure 5a). We used a photochemical box model that included a subset of the chemical reactions de-

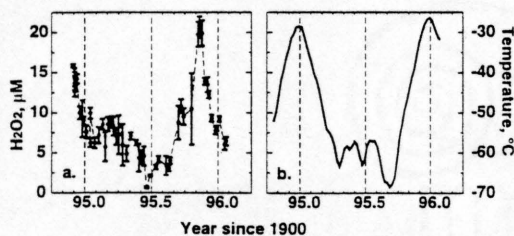


Figure 4. Measured concentrations of  $\text{H}_2\text{O}_2$  in surface snow (a) and computed surface snow temperature (b) at South Pole. Temperature estimates computed using an energy balance model [Liston, 1995] from measurements routinely collected by NOAA of air temperature, wind speed, and relative humidity.

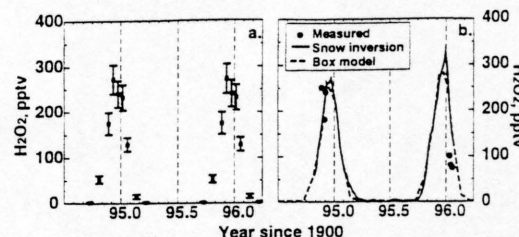


Figure 5. Atmospheric concentrations of  $\text{H}_2\text{O}_2$  at South Pole: (a) estimated from a photochemical box model using multi-year-averaged seasonal cycles in measured  $\text{O}_3$ , CO, temperature, relative humidity, and ozone burden; error bars represent expected variability from short term changes in these values; and (b) box model estimates extrapolated to the full annual cycle and using measured relative humidity, compared with the optimized inversion of the surface snow samples and atmospheric measurements.

scribed in Stewart and Thompson [1996]. Annual cycles for air temperature, pressure, relative humidity, actinic flux, carbon monoxide (CO), and surface ozone ( $\text{O}_3$ ) were taken from multi-year averages of measurements at South Pole. To our knowledge, no measurements of nitrogen oxide (NO) have been made so a concentration of 1 pptv was used throughout the year. In the model,  $\text{O}_3$ , CO, and NO were fixed and incident UV radiation computed using the latitude, time of year, and stratospheric ozone burden. Since  $\text{H}_2\text{O}_2$  concentration is highly sensitive to actinic flux and water vapor, the error bars on Figure 5a represent the expected range due to short-term variations in the most sensitive input variables.

Because measured relative humidity was significantly higher around the 1995 summer solstice than around the 1994 solstice, the measured relative humidity without multi-year averaging was used to model atmospheric  $\text{H}_2\text{O}_2$  for comparison to the snow inversion model results (Figure 5b).

### Inversion Model Results

A parameter search was conducted to estimate the snow-atmosphere partitioning relationship ( $K_D$ ). Using that reported by Conklin *et al.* [1993] resulted in atmospheric concentrations far higher than both observations and those predicted by the photochemical model. By comparing the estimate of the atmospheric concentration derived through surface snow inversion with that predicted by photochemical modeling, optimum parameters describing a quadratic shape of  $K_D$  relationship with temperature were determined. Note that the entire 14 month surface snow record was used to define that 3 parameters in the  $K_D$  relationship with temperature. The optimized annual atmospheric  $\text{H}_2\text{O}_2$  cycle was inverted from the snow concentrations shown on Figure 4 using a  $K_D$  double that given by Conklin *et al.* [1993] (Figure 1) and an effective snow grain radius of  $70 \mu\text{m}$  [Harder *et al.*, 1996] (Figure 5b).

## Discussion

The estimated annual atmospheric concentration cycle derived through inversion of the surface snow samples (Figure 5) is periodic and in good agreement with both photochemical model estimates and direct atmo-



spheric measurements made in late November and early December, 1994, although not with similar measurements made in January, 1996. During the latter period, there was significant local pollution from construction at the new Clean Air Facility at South Pole which may have reduced the measured levels of  $\text{H}_2\text{O}_2$  somewhat. In addition, a constant NO concentration was used throughout the year in the photochemical modeling. Higher NO levels later in the summer would decrease the atmospheric  $\text{H}_2\text{O}_2$  concentrations at that time, bringing the photochemical model and measurements into closer agreement. Atmospheric  $\text{H}_2\text{O}_2$  levels are strongly sensitive to water vapor mixing ratio and actinic flux. Both are strongly seasonal at South Pole and the former is approximately symmetric about the summer solstice while the latter is, at present, asymmetric because of the springtime stratospheric ozone hole. The photochemical model and surface snow inversion estimates suggest that a sharp, approximately symmetric peak in the atmospheric  $\text{H}_2\text{O}_2$  concentration ( $\sim 280$  pptv) occurs one to two weeks before the summer solstice while concentrations are very low ( $\sim 1$  pptv) throughout much of the winter.

The equilibrium snow-atmosphere partitioning relationship indicated in this study is greater than that previously reported from laboratory experiments. It should be noted, however, that only two individual laboratory experiments [Conklin *et al.*, 1993] were made at the very cold temperatures generally found at South Pole, primarily because response of the snow is so slow as to require experiments of very long duration. Hence, the laboratory-based equilibrium partitioning relationship is essentially an extrapolation from much warmer temperatures ( $-30^\circ\text{C}$  and  $-8^\circ\text{C}$ ). In addition, reinterpretation of the Conklin *et al.* [1993] data and incorporation of new laboratory data suggests that  $K_D$  is probably higher than previously thought [Winterle, 1996].

While the surface-snow concentration cycle is clearly not symmetric about the solstice, the estimated atmospheric cycle is approximately so, demonstrating that the bulk of this asymmetry about the solstice is due to the very strong temperature dependence in the uptake capacity of  $\text{H}_2\text{O}_2$  in snow. That is, the asymmetry in surface snow concentration is caused by the highly nonlinear, temperature dependent transfer function acting on a nearly symmetric atmospheric concentration, centered a few days to weeks before the solstice, and a symmetric surface temperature cycle that is centered about 10 days after the solstice.

## Conclusions

By comparing direct short term measurements and photochemical model predictions with estimates of the annual atmospheric  $\text{H}_2\text{O}_2$  concentration cycle that result from physically based inversion of surface snow sample concentrations, we conclude that surface snow acts as an excellent proxy for the annual atmospheric cycle. While this inversion of surface snow  $\text{H}_2\text{O}_2$  concentrations to an estimate of atmospheric loading is an important step toward the objective of inverting snow-pit and ice-core records into a long-term, interannual evaluation of atmospheric  $\text{H}_2\text{O}_2$  concentrations, it should be emphasized that transfer processes active beneath the surface have not been addressed here. To accomplish such an inversion will require a detailed understanding of the timing of accumulation at the core location and exchange between atmosphere and snow during burial. With no diel cycle, a long-duration, year-

around instrumental record of atmospheric chemistry and meteorology, and year-round access by winter-over personnel, South Pole is an ideal location for the study of atmosphere-to-snow transfer processes.

**Acknowledgments.** This work was supported by a NASA Graduate Fellowship for Global Change and in part by National Science Foundation's Office of Polar Program. Atmospheric photochemical modeling at NASA was supported by the Goddard Director's Discretionary Fund. Field work at South Pole was conducted under a cooperative agreement with the NOAA Climate Monitoring and Diagnostics Laboratory. We very much appreciate the help of K. McNitt and R. Ramos of NOAA/CMDL for their help in collecting samples at South Pole throughout the year and S. Oltmans and P. Novelli for access to the surface ozone and carbon monoxide data respectively.

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(Received October 22, 1996; revised January 13, 1997; accepted January 14, 1997.)

## **Appendix D**

### **Recent intra-annual snow accumulation at South Pole: Implications for ice core interpretation**

volume 102  
number D18

SEPTEMBER 27, 1997

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## Recent intra-annual snow accumulation at South Pole: Implications for ice core interpretation

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Department of Hydrology and Water Resources, University of Arizona, Tucson

**Abstract.** Spatial and temporal variability in snow accumulation can have a significant impact on interpretation of ice cores, particularly for chemical species that show a strong seasonal dependence either in atmospheric loading or in the atmosphere-to-snow transfer process. Using a unique, 7.25-year record of recent, year-round monthly snow accumulation at South Pole, we compute the number of years of averaging required to statistically ensure that an ice core record would have equivalent representation of snow from each month of the calendar year. For current South Pole meteorological conditions, averaging times of the order of 300 years are required to ensure equal representation of each month, with May being the least well-represented month. To ensure equal representation of 3-month seasons still requires averaging times of the order of 130 years. Through correlations of variability in monthly accumulation with potential snow transport by wind, we estimated a similar averaging time for Summit, Greenland. For studies of long-term, inter-annual changes in the atmospheric concentration of species that are reversibly deposited to snow such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), it is imperative that comparisons are made over intervals with equivalent representation of high versus low concentration periods. This is critical for  $\text{H}_2\text{O}_2$  because it has a very high annual variability in the surface snow, driven by photochemical and temperature cycles.

### Introduction

Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and other “reversibly deposited” chemical species of interest in ice core analysis show a strong seasonal dependence in atmospheric and/or surface snow concentrations. We use the term “reversibly deposited” to refer to species that are deposited as an impurity in the ice matrix but are sufficiently volatile to undergo postdepositional exchange with the atmosphere. Accumulation at polar ice coring sites can be highly variable in time and space, so an ice core record for these chemical species may reflect not only the interannual and intra-annual variations in the atmospheric concentration, but also a history of the season of snow accumulation for reversibly deposited species and a history of the season of deposition for irreversibly deposited species. Since interannual atmospheric loading is of primary interest in climate change studies, these subannual histories of accumulation and deposition can be considered to be “noise” on the ice core record. Because the intra-annual variation is often far larger than any expected long-term changes in atmospheric concentration [McConnell *et al.*, 1996], very large deviations in the ice core record, over both short

and long time sequences, can exist simply because of variations in the season of accumulation archived in the core [Steig *et al.*, 1994]. Multiple-year averages of ice core records are often used to mitigate this temporal and spatial accumulation variability, with typical averaging periods ranging from annual to century timescales [Stig and Neftel, 1991]. However, the averaging time required to sufficiently remove the potential impact of the subannual accumulation history is generally not known.

McConnell *et al.* [1997] reported year-round surface snow concentrations of  $\text{H}_2\text{O}_2$  at South Pole (Figure 1). Note that the peak snow concentration occurs in mid-November, well before the summer solstice. The overall  $\text{H}_2\text{O}_2$  variation in the surface snow is from over  $20 \mu\text{M}$  in mid-November to approximately  $2 \mu\text{M}$  around the winter solstice. In addition, the average concentration in the surface snow for November is nearly twice that for either October or December. Comparisons from year to year or between multiyear averages are only statistically reliable if high and low surface snow concentration periods are equally represented in each time range compared.

In this study, we use a multiyear record of recent, year-round monthly snow accumulation at 50 closely spaced stakes (Figure 2) at South Pole to derive quantitatively the averaging time required to statistically ensure that the snow accumulation record is filtered out of the chemical record, thereby revealing any significant long-term variations in surface snow concentrations. To

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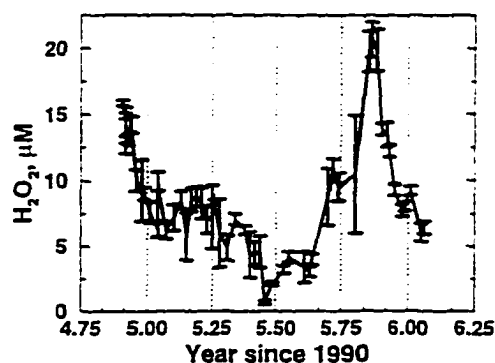


Figure 1. Hydrogen peroxide in surface snow at South Pole. Error bars represent 1 standard deviation.

our knowledge, this is the only accumulation record at any cold polar ice site of such long duration (7.25 years) and high time resolution (monthly throughout the year) that is replicated by a large number of stakes (50).

### Methods

We used a known statistical distribution to describe the monthly accumulation variability at the 50 stakes in the 0.3-ha study plot, located about 400 m grid east from the dome at Amundsen-Scott Station. This distribution was then used to compute the number of years that must be sampled (i.e., included in the average) in order to have, within some specified confidence interval, statistical assurance that the sample mean for a particular month is within a specified percentage of the underlying population mean or longer-term, spatially smoothed average accumulation for that month.

### Data

This work is based on data from a snow stake accumulation field that is approximately 50 m by 60 m in area with a stake separation of roughly 10 m in-line with the prevailing wind and 5 m in the crosswind direction (Figure 2). Monthly snow height measurements on each of the 50 stakes were made throughout the year by meteorological staff at South Pole. Snow height was measured relative to the tops of the ~1.5-m bamboo accumulation stakes to within ~0.15 cm, and the stakes were reset once or twice each year as snow accumulated. These simple month-to-month differences in the individual height measurements represent the gross accumulation at each stake. The continuous monthly record used in this analysis extends from September 1988 through December 1995. Occasional inaccurate resetting of an individual stake is probably the primary cause of uncertainty in the snow accumulation record, but the impact on the overall monthly accumulation histograms is negligible since each is made up of either 350 or 400 individual measurements.

If all values are summed and used simply as a mean monthly accumulation record, this array has an implicit

spatial wavelength window or band-pass region for horizontally propagating accumulation features given by  $nd$ , where  $n$  is the number of stakes in the in-line or cross-line direction and  $d$  is the respective stake spacing in meters. Spatial wavelengths shorter than this window, but still longer than twice the stake spacing (Nyquist sampling), will be strongly attenuated by the spatial array. For instance, long-wavelength perturbations in snow accumulation associated with airflow around the buildings at the Amundsen-Scott Station [Mosley-Thompson *et al.*, 1995] will not be attenuated by the spatial array, while the short-wavelength variations caused by sastrugi may be. An analysis of this sort that uses the individual stake data without summation can be biased by these long and short spatial wavelengths that have not been properly sampled and so lie outside of the array's band reject region [Telford *et al.*, 1976].

Monthly accumulation values were summed to define gross time-depth values at each stake. Since snow is often deposited and subsequently blown away, the gross time-depth maps were modified to keep only the oldest snow at each depth level (Figure 3) in the time-depth relationship. These modified time-depth relationships were then resampled to yield net or "preserved" monthly accumulation at each stake.

### Fitting Gamma Distributions to Preserved Monthly Accumulation

The gamma distribution is commonly applied in hydrology to describe the spatial distribution of precipitation. Individual storm events typically produce exponentially distributed rain gage data [Rice, 1988]. During a typical month, a number of individual storms may take place; so the monthly rain gage precipitation represents the sum of exponential distributions, which is a gamma distribution. While the concepts do not translate exactly to a snow environment because of wind redistribution of accumulating snow, we use gamma distributions to describe the always nonnegative preserved monthly accumulation values. A gamma distribution is

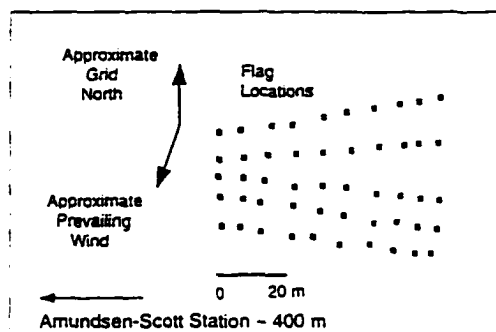


Figure 2. Map of the the snow stake accumulation field, which is located just outside of the clean air sector, about 400 m grid east of Amundsen-Scott Station, Antarctica.

## MCCONNELL ET AL.: INTRA-ANNUAL ACCUMULATION AT SOUTH POLE

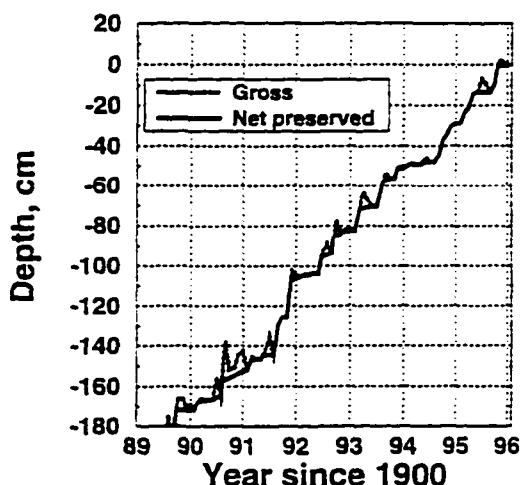


Figure 3. Time-depth map for an individual accumulation stake showing both gross monthly accumulation and net preserved accumulation.

defined by two parameters: the shape parameter  $\alpha$  and the scaling parameter  $\lambda$ . The distribution mean is given by  $\alpha/\lambda$  and the variance by  $\alpha/\lambda^2$ .

For a given distribution, the central limit theorem states that in the limit as the number of samples approaches infinity, the sample mean will approach the population mean and the sample mean distribution will be normally distributed [Rice, 1988]. For this analysis, the sample mean is the mean amount of snow that accumulated during the month in question within the entire averaging period. The population mean is that given by the gamma distribution fit to the available monthly accumulation data for all 50 stakes. Figure 4 shows the probability distribution of the sample mean as the number of samples (i.e., years averaged) increases. Note that the mode of the sample mean approaches the population mean as the number of samples increases and that the sample mean and mode rapidly converge, indicating that the sample mean distribution quickly approaches a normal distribution. Because the sample mean is essentially normally distributed, one can ensure that the sample mean is within a proportional error  $\epsilon$  of the population mean, with 95% confidence, by having the minimum sample size greater than

$$n = \left( \frac{2\sigma_r}{\epsilon m_r} \right)^2 \quad (1)$$

where  $m_r$  is the gamma distribution mean and  $\sigma_r$  is the standard deviation [Rice, 1988]. Also,  $n$  should be large enough to ensure normality of the sample mean by the central limit theorem, typically at least 30.

## Results

Histograms for all monthly accumulation values, both before and after modification to net or preserved accu-

mulation, are shown in Figure 5. Since the accumulation data are monthly, then this is the smallest time interval that can be evaluated with confidence. The preserved monthly data were classified by month and combined for all years and stakes to yield 350 to 400 samples for each month of the calendar year. Histograms of these monthly accumulation values are shown in Figure 6. Note that a time interval longer than a month might be used if the intra-annual variability in surface snow concentration for a chemical species can be readily classified by that longer time period. For example, seasons or 3-month periods might be suitable for a mostly irreversibly deposited species such as ammonium since month-to-month variability is not as high as for a photochemically produced species like  $H_2O_2$  (unpublished data).

Using a simple root-mean-square (RMS) minimization routine and constraining the distribution mean to be equal to the accumulation data mean, gamma distributions were fit to the individual monthly histograms of net accumulation (Figure 6). The resulting gamma distribution parameters, along with the mean and calculated standard deviation for each month, are given in Table 1. The gamma distribution parameters for each month were used in (1) to compute the required number of samples that must be averaged to ensure consistent representation of that month in the average for proportional error limits of 0.4, 0.2 and 0.1.

The averaging lengths reported in Table 1 indicate that, given current South Pole accumulation characteristics and for analyses involving chemical species that show strong month to month changes in atmospheric loading, a very long time-averaging window must be used when investigating interannual variability. To en-

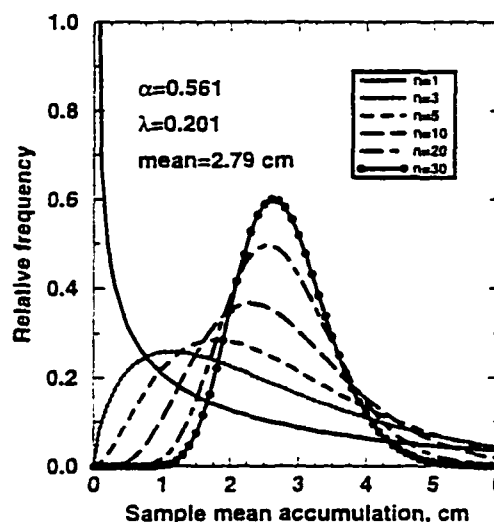


Figure 4. Distribution of the sample mean as the number of samples increases from 1 to 30. The shape  $\alpha$  and scaling  $\lambda$  parameters for the November gamma distribution were used for illustration (Table 1).

## MCCONNELL ET AL.: INTRA-ANNUAL ACCUMULATION AT SOUTH POLE

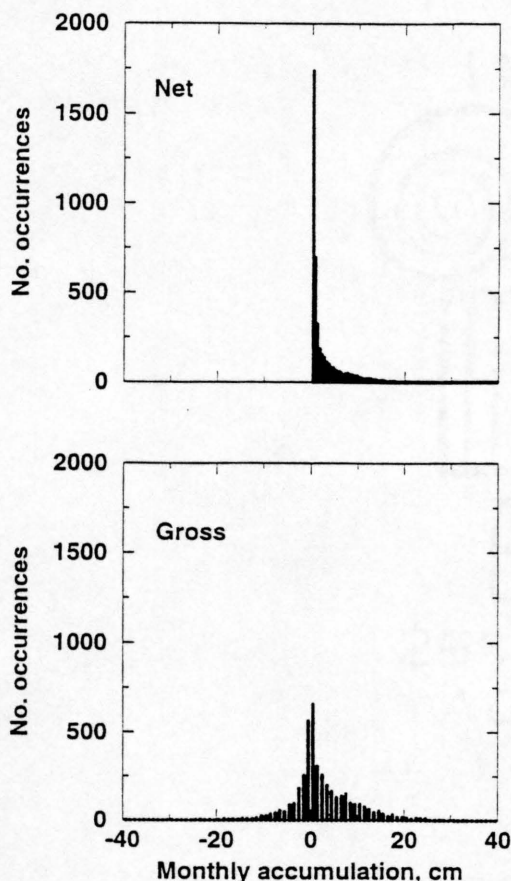


Figure 5. Histograms of gross and net preserved monthly accumulation for all 50 stakes and all measurement periods.

sure that each month within the year is adequately represented in a time average, the overall averaging time must be set to the largest value found for any individual month. For example, more than 310 years would be needed to include May accumulation for  $\epsilon = 0.2$ . Note that this is the averaging length for a single core. Averaging of adjacent cores would decrease the time window proportionally. That is, two adjacent cores combined would require half the averaging length. A similar, single core analysis was made for seasonal resolution for application to species with less month to month variability but still showing a strong annual cycle. Seasons were defined at South Pole as November, December, January for summer; February, March, April for autumn; etc. Averaging times to ensure consistent representation of each season within an averaging time window are reported in Table 2. As would be expected, required averaging times are less for seasonal than for monthly resolution, although the averaging times are still quite large (over 130 years for  $\epsilon = 0.2$ ). Note that as the resolution is lessened (e.g., month to season to year), the accumulation values become progressively more interdependent since depressions in the snow surface tend to fill in the next time period. Interdependence will result in an underestimate of the required number of averaging years. Note, however, that Palais *et al.* [1982] found no statistical correlation between surface form and annual accumulation at the Dome C site in Antarctica.

These averaging time estimates are for current accumulation conditions at South Pole. Different polar locations with different meteorology and snow accumulation characteristics will have different averaging times. Moreover, depositional conditions may have been different at South Pole in the past.

## Discussion

### Independence of Monthly Accumulation

This analysis assumes that monthly preserved accumulation values at each of the 50 stakes over the mul-

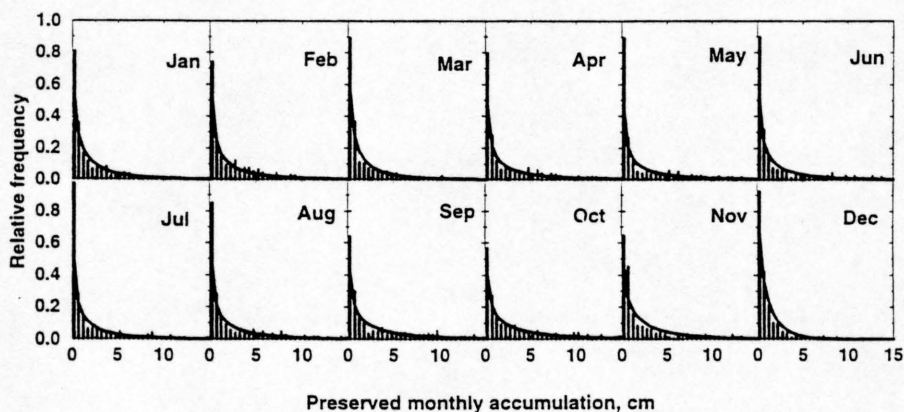


Figure 6. Monthly histograms of net preserved accumulation data for all 50 stakes. Solid lines are fitted gamma distributions.

## MCCONNELL ET AL.: INTRA-ANNUAL ACCUMULATION AT SOUTH POLE

**Table 1.** Monthly Accumulation Statistics and Fitted Gamma Distribution Parameters for South Pole and Computed Averaging Times for Three Proportional Error Limits  $\epsilon$ 

Month	Gamma Shape $\alpha$	Gamma Scaling $\lambda$	Mean $m_\gamma$ , cm	Standard Deviation $\sigma_\gamma$ , cm	Average Time $n$ , years		
					$\epsilon = 0.4$	$\epsilon = 0.2$	$\epsilon = 0.1$
Jan.	0.531	0.266	1.99	2.74	47	190	750
Feb.	0.421	0.192	2.19	3.38	60	240	950
March	0.461	0.266	1.74	2.56	54	220	870
April	0.371	0.138	2.68	4.40	68	270	1100
May	0.321	0.120	2.68	4.73	78	310	1200
June	0.401	0.184	2.18	3.44	62	250	1000
July	0.341	0.173	1.97	3.37	73	290	1200
Aug.	0.361	0.142	2.55	4.24	69	280	1100
Sept.	0.421	0.117	3.59	5.53	60	240	950
Oct.	0.471	0.125	3.77	5.50	53	210	850
Nov.	0.561	0.201	2.79	3.73	45	180	710
Dec.	0.690	0.540	1.28	1.54	36	150	580

Mean refers to gamma distribution mean.

tiyear record are essentially independent both in time and space. For example, November 1994 accumulation at stake 1 is assumed to be independent of November 1994 accumulation at all other stakes and to be independent of accumulation at stake 1 and all other stakes for November 1993.

The temporal independence criterion was investigated by plotting monthly accumulation at a stake  $n$  for a particular year  $y$  against accumulation at the same stake for the previous year,  $y - 1$ . No visual correlation was found. Similarly, the spatial independence criterion was tested by plotting monthly accumulation at one stake against monthly accumulation at a number of surrounding stakes. No significant correlation was found, perhaps because the stake spacing is somewhat random and, for the most part, larger than the dominant wavelength of the sastrugi. As a second test, the time series of monthly accumulation for each stake was cross-correlated against time series for adjacent stakes, and, except for evidence of the annual accumulation cycle, again, no strong correlation between adjacent stakes was seen.

#### Interannual Accumulation

The mean monthly accumulation derived from the snow stake data used in this study is 2.44 cm of surface snow. Assuming a surface snow density of 0.35 g

cm<sup>-3</sup> [Mosley-Thompson *et al.*, 1995] yields 10.3 cm of water equivalent per year. This annual accumulation rate is well within the range of reported regional values for this time period at South Pole [Mosley-Thompson *et al.*, 1995], although slightly higher than the reported transect values for accumulation approximately 1 km from the South Pole Station. Note, however, that a trend toward increasing recent accumulation has been reported and that the published transect values are for an earlier time period of 1978 through 1990. The agreement between the previously reported net annual accumulation rates and those from the accumulation stake array suggests that the array has no discernible local snow-trapping effect. The monthly mean accumulation and standard deviations listed in Table 1 demonstrate that, while highly variable, the maximum accumulation at South Pole occurs in spring (September/October), with summer (December/January) having relatively little accumulation.

Since this current study examines spatial variability over relatively short distances (meters to tens of meters) and over short time periods (months to seasons), we have not considered any possible influence of the South Pole Station buildings and structures on the local, long-term accumulation. Variability within these distances and times is primarily determined by peak wind velocities. While it seems unlikely that our findings would be significantly affected by the long-wavelength accumula-

**Table 2.** Seasonal Accumulation Statistics and Fitted Gamma Distribution Parameters for South Pole and Computed Averaging Times for Three Proportional Error Limits  $\epsilon$ 

Season	Gamma Shape $\alpha$	Gamma Scaling $\lambda$	Mean $m_\gamma$ , cm	Standard Deviation $\sigma_\gamma$ , cm	Average Time $n$ , years		
					$\epsilon = 0.4$	$\epsilon = 0.2$	$\epsilon = 0.1$
NDJ	0.761	0.125	6.10	6.99	33	130	520
FMA	1.431	0.217	6.61	5.53	18	70	280
MJJ	1.011	0.148	6.83	6.79	25	99	400
ASO	1.441	0.151	9.56	7.97	18	69	280

Seasons are defined as NDJ, November, December, January; FMA, February, March, April; MJJ, May, June, July; and ASO, August, September, October.



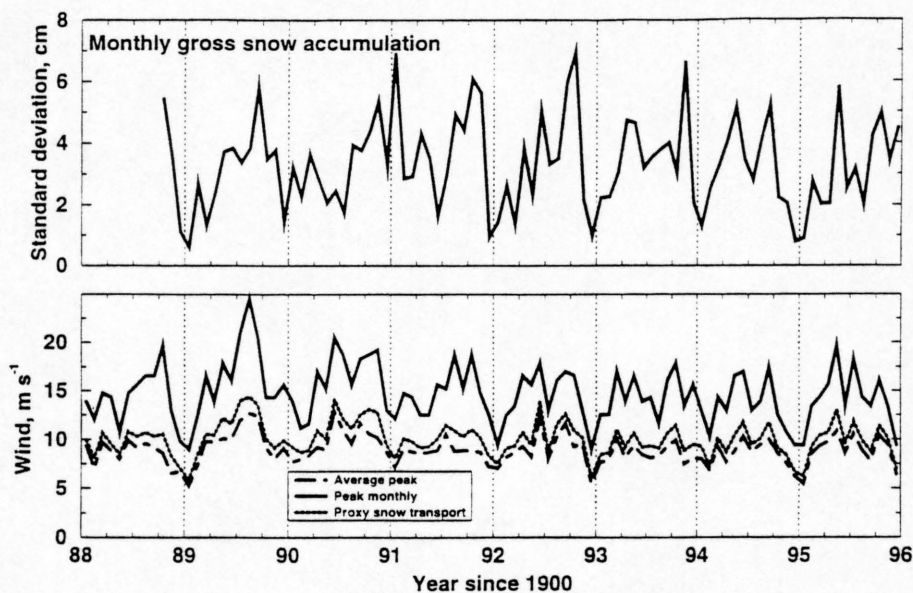


Figure 7. Standard deviation of gross monthly accumulation over the 50 accumulation stakes and corresponding monthly maximum winds.

tion perturbation of the nearby Amundsen-Scott Station, such trapping of snow by the station would likely decrease local wind speeds and increase net accumulation, making the averaging time estimates computed here shorter than what would be required farther away from the station.

#### Extension to Other Polar Ice Coring Sites

Wind velocities at South Pole are quite high, particularly during winter months, and we hypothesize that the very large stake-to-stake variability in monthly accumulation is primarily caused by these high winds since snow transport is highly dependent on wind speed [Pomeroy and Jones, 1996; Pettre et al., 1986]. The standard deviation in gross monthly accumulation is plotted in Figure 7, along with two indicators of windiness during each accumulation month. The average peak wind is the simple average over the month of the peak wind velocity recorded for each day. The peak monthly wind is the maximum wind reported for any day during the month. Note the obvious correlation of monthly accumulation variance to both peak wind speed indicators.

Investigations of transport of snow by wind in polar environments have found that the mass of snow transported is empirically related to the wind speed at 10 m height raised to the power 4.2 [Pomeroy and Jones, 1996]. If the stake-to-stake variability in snow accumulation is related to transport by wind, then there should be a correlation between wind speed raised to the power 4.2 and the standard deviation of the monthly accumu-

lation. The peak wind speeds reported for each day were raised to the power 4.2, averaged over the month, and the average raised to the power 1/4.2 to create a proxy snow transport time series  $U_{\text{proxy}}$  during the time period covered by the accumulation record. This proxy record, also plotted in Figure 7, shows a similar correlation with accumulation variance. In Figure 8, the standard deviation in monthly net accumulation is plotted against monthly proxy snow transport and a function of the form  $\sigma = AU_{\text{proxy}}^{4.2}$  fitted to the data. Note that the function approximates the accumulation data, confirming that the stake-to-stake variation in snow accumulation at South Pole is indeed correlated to snow transport by wind.

For potential ice coring sites with lower peak winds, the variance in monthly accumulation from location to location and from year to year should be significantly less. If we make the assumption that the stake-to-stake monthly accumulation variance to peak daily wind speed relationship at South Pole (Figure 7) has general application in polar environments, then it is possible to extend these averaging results to other ice core sites. Using ~2-m wind speeds from the automatic weather station at Summit, Greenland [Stearns et al., 1993], to estimate the potential monthly transport of snow by wind, we derived the monthly standard deviations shown in Table 3. Note that in using the ~2-m wind speed without correction to 10 m, we may have underestimated the standard deviation at Summit to some degree. Because the surface roughness over snow is generally  $\leq 0.1$  cm [Lettau, 1969], the differences from ~2 to 10 m are relatively small. Snow accumulated during

## MCCONNELL ET AL.: INTRA-ANNUAL ACCUMULATION AT SOUTH POLE

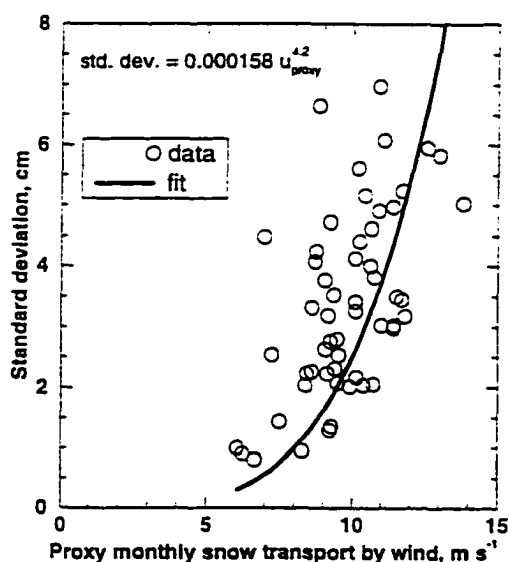


Figure 8. Standard deviation of gross monthly accumulation over 50 accumulation stakes (June 1991 through December 1995) plotted against a proxy record of snow transport by wind during each accumulation month.

the measurement period, so 2 m is only an approximation for the Summit wind speed measurement height. Again, because of the low surface roughness, the difference in 1.5- and 2.5-m wind speeds is < 10%.

Estimates of the intra-annual precipitation over central Greenland based on regional scale meteorology [Bromwich *et al.*, 1993] suggest that maximum precipitation occurs in late summer to early autumn and a minimum in late winter to early spring, with approximately twice the accumulation rate at the maximum than at the minimum. Analyses coupling passive microwave data with local air temperature and high-resolution  $\delta^{18}\text{O}$  profiles

in the snow pack to estimate the timing of accumulation at Summit [Shuman *et al.*, 1995] found, although highly variable, an annual accumulation cycle with similar peak/trough timing but an amplitude of the cycle less pronounced than that suggested by the Bromwich *et al.* [1993] regional analysis. We approximated the monthly precipitation as a sinusoid with peak timing as described above, an amplitude giving twice as much accumulation at the maximum as at the minimum, and a monthly mean of  $5 \text{ cm yr}^{-1}$  (Table 3), yielding a total of  $60 \text{ cm yr}^{-1}$  (H. Kuhns, personal communication, 1996). Again, using (1), we computed the required averaging time for proportional error limits of 0.4, 0.2, and 0.1 percent for Summit (Table 3). Averaging times are much lower than for South Pole when precipitation is high and wind speeds are low. However, peak wind speeds at Summit are higher than at South Pole and precipitation may be near a minimum during the month of strongest winds (March), leading to a long averaging time of the order of 300 years for that month (for  $\epsilon = 0.2$ ).

### Conclusions

There are important differences in the implications of these findings for interpretation of irreversibly versus reversibly deposited species in ice cores. The timing of deposition should be more important for irreversibly deposited species, e.g., aerosol-associated cations and sulfate. On the other hand, postdepositional exchange is at least as important as deposition for reversibly deposited species in determining concentrations buried and thus preserved in firn/ice. The timing of accumulation determines the extent of postdepositional exchange.

Averaging times of the order of 300 years may be somewhat larger than would be required at other ice core sites, at least in part because of the moderately high winds and low to moderate accumulation rates found at South Pole. Extension of these results to conditions at Summit, Greenland, suggests that for many months, much lower averaging times are adequate; although the longest averaging time (March) is similar to

Table 3. Estimated Monthly Accumulation Statistics for Summit, Greenland, and Computed Averaging Times for Three Proportional Error Limits  $\epsilon$

Month	Wind Transport $U_{\text{proxy}}$	Standard Deviation $\sigma_{\text{m}}$ , cm	Mean $m_{\text{m}}$ , cm	Average Time n, years		
				$\epsilon = 0.4$	$\epsilon = 0.2$	$\epsilon = 0.1$
Jan.	9.38	1.9	3.6	7	30	110
Feb.	11.12	3.9	3.4	30	130	530
March	12.43	6.2	3.6	70	300	1200
April	9.00	1.6	4.2	4	20	60
May	8.10	1.0	5.0	1	4	20
June	8.50	1.3	5.8	1	5	20
July	7.94	1.0	6.4	1	2	8
Aug.	7.81	0.9	6.7	1	2	8
Sept.	8.46	1.2	6.4	1	4	20
Oct.	9.56	2.1	5.8	3	13	50
Nov.	10.35	2.9	5.0	9	30	140
Dec.	11.62	4.7	4.2	30	130	500



## MCCONNELL ET AL.: INTRA-ANNUAL ACCUMULATION AT SOUTH POLE

South Pole. While annual accumulation at Summit is nearly double that at South Pole, peak wind velocities are often higher and precipitation may be at a minimum during the month of highest wind speeds. Ice coring sites with more annual accumulation and/or lower peak wind velocities would have lower required averaging times. On the other hand, for very low accumulation sites like Vostok, required averaging lengths are probably much greater since the minimum number of samples in the averaging length is related to the mean accumulation raised to the power -2.

An intra-annual accumulation study of this type would not have been possible without the year-round monthly accumulation data. South Pole is the only potential polar ice coring site that is occupied year-round, so it is the only place where a long-term, high time resolution, multiple-stake accumulation record of this type can be collected at this time. We very strongly encourage the continued maintenance of this unique record, both for intra-annual accumulation studies and for atmosphere-snow transfer studies in general.

**Acknowledgments.** This work was supported by the National Science Foundation's Office of Polar Programs, a NASA Graduate Fellowship for Global Change, and a cooperative agreement with the NOAA Climate Monitoring and Diagnostics Laboratory. Special thanks to K. Sharp, V. Campbell, and D. Fischer of Antarctic Support Associates for their help in obtaining the snow accumulation data and to K. McNitt, R. Ramos, and T. Swanson of NOAA for much appreciated field support at South Pole. Thanks also to C. Stearns for access to the AWS data at Summit.

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(Received June 18, 1996; revised February 21, 1997; accepted March 11, 1997.)

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