A lumped parameter model for the atmosphere-to-snow transfer function for hydrogen peroxide

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Abstract. Of the main atmospheric oxidants, only hydrogen peroxide (H$_2$O$_2$) 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$_2$O$_2$ and those preserved in the ice core. Snow-pit H$_2$O$_2$ 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 firm. 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 [Conklin 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$_2$O$_2$ between near surface snow and the atmosphere, allowing already buried snow to either take up or release H$_2$O$_2$ 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$_2$O$_2$ concentration in the past from snow-pit and ice-core records and (2) to invert snow-pit and ice-core H$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_2$), is an important key to understanding past and future global climate change. Of these primary oxidants, only H$_2$O$_2$ 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 firm and ultimately the ice core [Thompson, 1995]. The incorporation of H$_2$O$_2$ into firm 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 δ$^{18}$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$_2$O$_2$. Beier et al. [1991] evaluated the seasonal variation of a number of chemical species (¹⁰⁷Be, Cl$^-$, SO$_4^{2-}$, H$_2$O$_2$, ²¹⁰Pb, mineral dust, and δ$^{18}$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 as-

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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$_2$O$_2$ or δ$^{18}$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$_2$O$_2$ concentration at the time of snow accumulation. Conversely, for a strongly seasonally dependent chemical species such as H$_2$O$_2$, the transfer function can be used to invert the H$_2$O$_2$ profile with depth into an estimate of the snow accumulation pattern at the particular pit or core location, if assumptions about the atmospheric H$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_2$ during the year, a relatively simple five-parameter model would be adequate to simulate concentrations of H$_2$O$_2$ in near surface snow and buried snow/firn.

Model

Our snowpack model includes (1) a transfer-function component to relate atmospheric H$_2$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 H$_2$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 H$_2$O$_2$ is scavenged by liquid particles (e.g., rime formation) [Sigg and Neftel, 1988]. Co-deposition refers to equal rate of condensation of H$_2$O and H$_2$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, H$_2$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 H$_2$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 H$_2$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., 1992; Führer 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 H$_2$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 H$_2$O$_2$ at equilibrium:

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

where $C_{\text{snow}}$ is the equilibrium concentration (moles per liter) of H$_2$O$_2$ in surface snow, $C_{\text{air}}$ is the concentration (atmospheres) of H$_2$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 H$_2$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:
\[ Q = 1.0 + \frac{dz}{dl} S_{eq} \]  

(2)

where \( \frac{dz}{dl} \) 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 \( H_2O_2 \) partitioning ratio:

\[ \frac{C_{snow}}{C_{air}} \text{ effective} = Q \frac{C_{snow}}{C_{air}} \text{ equilibrium} \]  

(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 et al., 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

\[ C_{i,t} = M C_{i=0,t} + (1 - M) C_{i,t-1} \]  

(4)

where \( C_{i,t} \) is the effective snow equilibrium concentration of \( H_2O_2 \), \( i \) 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

\[ M = \exp \left( \frac{-z_i}{t \tau_{fold}} \right) \]  

(5)

where \( z_i \) is the buried layer depth relative to the surface and \( \tau_{fold} \) (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 \( H_2O_2 \) in the firm [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 \( \delta^{18}O \) diffusion and so computed the diffusivity of \( \delta^{18}O \) 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 \( H_2O_2 \) signal in recent snow and at depth with diffusion backed out that the effective diffusivity of \( H_2O_2 \) is about 1.5 to 1.75 that of \( \delta^{18}O \), reflecting a lower uptake capacity of the snow for \( H_2O_2 \) than for \( \delta^{18}O \).

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 \( H_2O_2 \) profile to that measured in the Eurocore in 1988 [Sigg and Neftel, 1988], we computed an \( H_2O_2 \) to \( \delta^{18}O \) 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 \( H_2O_2 \) concentration consistent with the chosen model parameters \( A, B, C \) and \( S_{eq} \). After accumulation, the modeled \( H_2O_2 \) concentration changes according to the rate of burial, the surface conditions during the early stages of burial, and the model parameter \( \tau_{fold} \). The layer compacts following the depth-density relation observed 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°C and has a mean of -31°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 \( H_2O_2 \) concentration, and the surface air temperature during the sim-
ulation. 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° 58' N, 38° 46' 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 K (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 a MS25 solid state multiplexer. The data logger and multiplexer 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 CO$_2$ at 15°C using 2 mL meltwater samples in an automated CO$_2$-H$_2$O equilibration unit coupled to a Delta-S gas ratio mass spectrometer. H$_2$O$_2$ analyses were done as described previously [Bales et al., 1995b].

Results

Field Measurements

The H$_2$O$_2$ and $\delta^{18}$O profiles showed distinct differences between pits, with much of the difference due to when snow accumulated at each site. The measured H$_2$O$_2$ and $\delta^{18}$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 H$_2$O$_2$ concentration [Bales and Choi, 1996]. The i-day average of the measured atmospheric H$_2$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, measured and modeled values were in approximate agreement [Bales et al., 1995; Neftel, 1996; Führer et al., 1996]. Note that on a timescale, the overall shapes of the annual H$_2$O$_2$ and $\delta^{18}$O profiles were quite similar between all three pits. One remaining difference is the higher H$_2$O$_2$ values in the thermocouple string pit in late summer and early fall 1994.

The summer peaks in $\delta^{18}$O were much broader than those for H$_2$O$_2$ and extended well into the autumn. Because the H$_2$O$_2$ signal reflects both the depositional temperature and the atmospheric H$_2$O$_2$ concentration,
Figure 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.

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 well as $\text{H}_2\text{O}_2$.

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 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 $A$, $B$, $C$, $z_e$, 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 $H = 0.0$, $C = 3.75$. 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,

\[ T = (\delta^{18}O + 18.2)/0.53, \]

where $\delta^{18}O$ is in per mil.

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

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

**Figure 6.** Log concentration ratios for $H_2O_2$ as a function of temperature resulting from parameter estimation using the automatic depth gage snow-pit data. For all three cases, the surface interaction ($z_{eq}$) and disequilibrium terms ($S_{eq}$) were 0.72 m yr$^{-1}$ and 1.05 yr m$^{-1}$ respectively. Laboratory equilibrium, co-deposition, and ADG effective equilibrium lines are from Figure 1.
Figure 7. Modeled H$_2$O$_2$ profiles with depth for the three ADG pits: (a) Kenton AWS, (b) GISP2 AWS, and (c) GISP2 thermocouple pits.

tween the GISP2, thermocouple and laboratory equilibrium relationships, although the Kenton estimate was not as consistent.

The modeled snow-pit profiles for H$_2$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.

Discussion

In our five-parameter model, we assumed that pit-to-pit differences in H$_2$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 H$_2$O$_2$ concentrations throughout the year. There is a strong positive correlation between accumulation rate and H$_2$O$_2$ concentration; that is, a short-term increase in accumulation rate leads to a short-term increase in preserved H$_2$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 $\delta^{18}$O profile and suggests a transfer function for $\delta^{18}$O that is to some degree a function of accumulation rate. For ice cores we must rely on $\delta^{18}$O implied temperatures to interpret the H$_2$O$_2$ profile, so understanding any $\delta^{18}$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 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 m yr$^{-1}$. For a 30 layer per year model ($t = 0.033$ years), the average c folding depth of surface interaction when $z_{c, fold} = 0.72$ m yr$^{-1}$ is 0.024 m. Similarly, the average value for Q when $S_{eq} = 1.05$ 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 H$_2$O$_2$ when Q = 1.64 and $t = 0.033$ years.

Laboratory studies show that, at -15 °C, snow will release about 85% of its excess H$_2$O$_2$ after 0.033 years. Note that the majority of the snow represented in the pits accumulated when air temperatures were about -15 °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 H$_2$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 H$_2$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 H$_2$O$_2$ concentration by 50%. Sporadically varying accumulation (Figure 8d) resulted in a much less uniform H$_2$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

Figure 8. Example synthetic snow-pit H$_2$O$_2$ profiles with various accumulation histories: (a) uniform at 60 cm yr$^{-1}$, (b) uniform at 30 cm yr$^{-1}$, (c) uniform at 120 cm yr$^{-1}$, and (d) sporadic around 60 cm yr$^{-1}$. The dashed line is the pit average concentration.
for the thermocouple and Kenton, then seasonality in the parameters \( S_{eq} \) and \( Z_{fold} \) 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 the 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 \( \text{H}_2\text{O}_2 \) 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, 1969], as a means of estimating accumulation timing. These studies rely primarily on hoar layers and 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 \( \text{Ca}^{2+} \), \( \text{NH}_4^+ \), \( \text{NO}_3^- \), 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. \( \text{Ca}^{2+} \), \( \text{NH}_4^+ \), and MSA are aerosol-associated species, transported to an ice-core site from lower latitudes, and once deposited are relatively immobile in the snow/firm. Concentrations deposited in the snow depend largely on atmospheric concentrations rather than on temperature. \( \text{NO}_3^- \) 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 \( \delta^{18}\text{O} \) 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 \( \text{H}_2\text{O}_2 \) concentration, \( \text{H}_2\text{O}_2 \) can be used to reconstruct the accumulation history. \( \text{H}_2\text{O}_2 \) 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 \( \text{H}_2\text{O}_2 \) cycle is preserved, it may also be possible to identify and deconvolve multiyear accumulation seasonality shifts in situations where the seasonal \( \text{H}_2\text{O}_2 \) cycle does not survive diffusional smoothing. For coupled \( \text{H}_2\text{O}_2 \) and \( \delta^{18}\text{O} \) 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 \( \text{H}_2\text{O}_2 \) (Figure 1) and lower \( \delta^{18}\text{O} \) 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 \( \text{H}_2\text{O}_2 \) 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 \( \mu \text{M} \) 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 \( \text{H}_2\text{O}_2 \) 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 \( \text{H}_2\text{O}_2 \) will make possible inver-
sion of ice-core records to local H$_2$O$_2$ 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$_2$O$_2$ record.

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