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**Recommended Citation**  
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Diel variations of H$_2$O$_2$ in Greenland: A discussion of the cause and effect relationship


Abstract. Atmospheric hydrogen peroxide (H$_2$O$_2$) measurements at Summit, Greenland, in May-June, 1993 exhibited a diel variation, with afternoon highs typically 1–2 parts per billion by volume (ppbv) and nighttime lows about 0.5 ppbv lower. This variation closely followed that for temperature; specific humidity exhibited the same general trend. During a 17-day snowfall-free period, surface snow was accumulating H$_2$O$_2$, apparently from nighttime cocondensation of H$_2$O and H$_2$O$_2$. Previous photochemical modeling (Neftel et al., 1995) suggests that daytime H$_2$O$_2$ should be about 1 ppbv, significantly lower than our measured values. Previous equilibrium partitioning measurements between ice and gas phase (Conklin et al., 1993) suggest that air in equilibrium with H$_2$O$_2$ concentrations measured in surface snow (15–18 μM) should have an H$_2$O$_2$ concentration 2–3 times what we measured 0.2–3.5 m above the snow surface. A simple eddy diffusion model, with vertical eddy diffusion coefficients calculated from balloon soundings, suggested that atmospheric H$_2$O$_2$ concentrations should be affected by any H$_2$O$_2$ degassed from surface snow. However, field measurements showed the absence of either high concentrations of H$_2$O$_2$ or a measurable concentration gradient between inlets 0.2 and 3 m above the snow. A surface resistance to degassing, that is, slow release of H$_2$O$_2$ from the ice matrix, is a plausible explanation for the differences between observations and modeled atmospheric profiles. Degassing of H$_2$O$_2$ at a rate below our detection limit would still influence measured atmospheric concentrations and help explain the difference between measurements and photochemical modeling. The cumulative evidence suggests that surface snow adjusts slowly to drops in atmospheric H$_2$O$_2$ concentration, over timescales of at least weeks. The H$_2$O$_2$ losses previously observed in pits sampled over more than 1 year are thought to have occurred later in the summer or fall, after the May-July field season.

Introduction

Hydrogen peroxide (H$_2$O$_2$) archived in polar ice cores offers the potential to help constrain model estimates of atmospheric hydroxyl radical (OH) concentrations in the past. Recent attempts to use the H$_2$O$_2$ records in ice cores have assumed that concentrations found in the ice are related to those in the atmosphere at the time of deposition [Sigg and Neftel, 1991; Thompson et al., 1993] by a linear function that is constant over time. However, the atmosphere snow “transfer function” is neither constant over time nor linear; it depends on processes controlling H$_2$O$_2$ deposition, on postdepositional air-snow exchange, and possibly on chemical reactions in buried snow/ice [Neftel et al., 1995].

The first continuous H$_2$O$_2$ gas phase observations at Summit, Greenland, were made by Sigg et al. [1992] in summer, 1990. They showed surprisingly high gas phase concentrations during midday, which were more than double the concentrations predicted from photochemical model calculations [Neftel et al., 1995]. In addition, a strong diel variation was apparent, with the lowest values from midnight to early morning. Sigg et al. [1992] suggested that the polar snow surface acts as a temporary storage for H$_2$O$_2$ at night. Neftel et al. [1995] also suggested that degassing of H$_2$O$_2$ from the snowpack could explain the discrepancy between the measured and predicted gas phase concentrations.
The purpose of the work reported here was to test the hypothesis that on a daily basis, the surface snow is a temporary storage reservoir for H$_2$O$_2$, and that surface snow readily exchanges H$_2$O$_2$ with the atmosphere. We report experimental and monitoring results from field work at Summit, Greenland, during summer, 1993.

**Methods**

These studies were carried out at the Greenland Ice Sheet Project 2 (GISP2) camp at Summit, Greenland (72° 58' N, 38° 46' W), in May through July of 1993. (Note that at the summer solstice, solar zenith angles range from 50° at noon to 83° at midnight.) We measured H$_2$O$_2$ in the air at 0.2, 3, and 3.5 m above the snow and in surface snow. Because of logistical constraints, experimental investigations of the transfer function at most polar sites are currently possible only during summer months. Therefore responses of the snowpack to atmospheric concentrations could be observed over only a very limited range of atmospheric concentrations and for short times.

The atmospheric H$_2$O$_2$ detector involved drawing sample air and pumping H$_2$O$_2$-free water into a coil scrubber, where all of the H$_2$O$_2$ was transferred from the air to the water; the H$_2$O$_2$ content of the water was then analyzed using a peroxydase method [Sigg et al., 1992]. Tubing and parts in contact with H$_2$O$_2$ containing fluids were perfluoroalkoxy (PFA) teflon or glass, plus a short length of peristaltic pump tubing that was tygon. Inlet lines were 8-mm ID PFA teflon. The detector automatically switched between H$_2$O$_2$-free air and sample air on a cycle of 6 to 20 min.

During most of the sampling period, one atmospheric detector system was located in a heated canvas laboratory building, with the sampling line extending outside to a height of 1 m above the building (3.5 m above snow surface). Line losses in this system (~3.5 m length) were estimated to be insignificant, based on a one-time measurement of a gas calibration source near the end of the sampling period. We also checked for line losses earlier by comparing measurements with and without the sampling tube; differences were insignificant. On a few of the days we moved the system outside to make side-by-side comparisons with a second system that was in a heated box located 100 m from the laboratory. The second system drew air through inlet tubes at 0.2 and 3 m sequentially during each cycle. Line losses in the second system were estimated to be 20-30%, based on three calibration measurements.

Micrometeorological data were taken from an automatic weather station [Stearns et al., 1993], located approximately 500 m from the building and H$_2$O$_2$ sampling site (GISP2 AWS). Air temperature was measured at 0.2 and 1.8 m above the snow, and relative humidity, air pressure, wind direction, and wind speed were measured at 2 m above the snow surface. Because of instrument problems, relative humidity data were taken from a second micrometeorological station, which was located at the atmospheric sampling camp 30 km south of the GISP2 camp (Kenton AWS). Other measurements taken at both stations matched well.

Daily surface snow samples were collected at the atmospheric sampling camp; collection time depended on the availability of personnel. Five replicates were taken from the entire surface snow layer, defined by visual observation of grains and layering. The still-frozen samples were brought to the GISP2 camp, melted, and analyzed as soon as possible after melting; usually within 1 hour. Analyses were done on an instrument with the same design as used for the atmospheric measurements; the air pump was shut off and liquid samples were injected directly at the outlet of the coil (beginning of the liquid sampling loop). Aliquots were refrozen and analyzed in our laboratory in Tucson 3 months later, with comparable results. This lack of H$_2$O$_2$ loss is in contrast to sample handling methods used on other studies, where losses during transport were observed (unpublished data).

We collected depth samples of the top surface of the snow near the GISP2 camp by sequentially scraping a few tenths of a millimeter of water equivalent (few millimeters of snow) from a 10 x 10 cm area of the snow surface into a sampling container. Depths sampled were estimated from sample weights. Samples were generally melted and analyzed within 1 to 3 hours after collection. These are referred to as micropits.

Fog and fresh snow samples were collected on polyethylene trays set on poles 1 m above the snow. Trays were about 150 m upwind from the GISP2 drilling dome. Fog or snow was allowed to accumulate overnight and scraped into bottles at about 0630-0700 UT. Sample handling and analysis were as for the surface snow samples.

A balloon was used to make soundings of atmospheric pressure, wind speed and temperature at least twice daily, up to a height of 700-800 m.

**Results**

To evaluate H$_2$O$_2$ exchange between surface snow and the atmosphere, we focus on the first 17 days, when there were no major storms. Regular balloon soundings were made during these days as well. Hourly means of H$_2$O$_2$ measured in the atmosphere during summer 1993 are displayed in Figure 1a. They show a similar pattern as that reported by Sigg et al. [1992], with daytime highs generally between 1.0 and 2.0 parts per billion by volume (ppbv) and nighttime minima about 0.5 ppbv lower. H$_2$O$_2$ in surface snow showed a small but statistically significant increase over this 17-day period, from 15 to 18 uM (Figure 1b). The average daily increase and standard error were 0.18 ± 0.05 uM.

The diel variation in H$_2$O$_2$ was found to closely follow that for temperature (c.f. Figure 1a versus 1c). Relative humidity reflected a daytime low of 10-20%, and a nighttime high of 60-80% (data not shown). Diel changes in specific humidity were also apparent, and followed a diel cycle (Figure 1d). Values reached a maximum late in the evening and a minimum during the late morning hours.
A linear regression of $\text{H}_2\text{O}_2$ concentration as a function of temperature for the 17-day period shown on Figure 1 gave a standard error of 0.203; the standard error was 10% lower (0.183) with atmospheric pressure and specific humidity as additional dependent variables (Figure 2). Average $\text{H}_2\text{O}_2$ concentration for the period was $1.0 \pm 0.4 \text{ ppbv}$, average temperature was $-16^\circ\text{C}$, and average specific humidity was $0.6 \pm 0.4 \text{ g kg}^{-1}$ (± standard deviation). For the period after day 167, the correlations were not as good, probably due to the highly variable weather and frequent snowfall (R. Bales, unpublished data, 1994). However, the daily trend in atmospheric $\text{H}_2\text{O}_2$, both for the period shown and later days, did closely follow changes in air pressure (Figure 1e), suggesting that shifts in sources of air masses were important. Winds were out of the south (southeast to southwest) for the entire period (data not shown). Applying the same regression to the only previous continuous $\text{H}_2\text{O}_2$ data for Summit, the 1990 data of Sigg et al. [1992] and the Kenton AWS data, gave similar results (Figure 3). That is, atmospheric $\text{H}_2\text{O}_2$ variations closely followed changes in air temperature, specific humidity, and pressure.

During the 17-day period in 1993, the inversion height varied from 20 to 240 m, with an average of 150 m (excluding seven soundings with no inversion) (Figure 1g). The atmosphere below the inversion height on average contained about 4.2 $\mu\text{mol m}^{-2}$ of $\text{H}_2\text{O}_2$ (at 1.0 ppbv). The average surface snow $\text{H}_2\text{O}_2$ concentration for the same period was 16.3 $\mu\text{M}$, or 16.3 $\mu\text{mol m}^{-2} \text{mm}^{-1}$.
Thus the top 0.26 mm of water equivalence (~2.6 mm snow) contained as much H_2O_2 as the entire atmosphere below the average inversion height.

The average amount of water contained in the atmosphere below the inversion height was 82 g m^-2 for the period, or 0.082 mm. Thus a day-to-night change in specific humidity of only 50%, typical for the period, represents the top 0.04 mm of water (~0.4 mm snow). From visual observations of the surface snow each morning, it was apparent that there was hoar and/or rime deposition nearly every night. Further, there was fog deposition in the night and early morning of days 154 and 160 (equivalent to 0.097- and 0.194-mm water, respectively).

Micropits showed that maximum H_2O_2 concentrations were at the top with lower concentrations below the surface snow. That is, the gradient of H_2O_2 was into, rather than out of the snow (Figure 4). There was a remarkable consistency among surface samples taken at different times with little temporal variation. We attribute differences between sample collections at different times to spatial variability rather than to changes
in the surface snow. Micropit H$_2$O$_2$ concentrations were within a few percent of surface layer H$_2$O$_2$ concentrations shown on Figure 1b.

Wind data from 0.25- and 3.0-m heights at Summit were used to infer the aerodynamic roughness length $z_0$ and friction velocity $u_*$. The wind data consisted of scalar-averaged measurements of wind velocity over 15-min time intervals. The roughness length was computed from:

$$\ln(z_0) = \frac{u_s}{u_*} \left( \ln(z_1) - \ln(z_2) \right)$$

(1)

where $z_1$ and $z_2$ are the measurement heights of 0.25 and 3.0 m, and $u_1$ and $u_2$ are the respective wind measurements. This definition follows from the well-known logarithmic wind profile equation

$$u_i = u_* \kappa^{-1} \ln \frac{z_i}{z_0}$$

(2)

where $\kappa$ is the von Karman constant, taken to be 0.4. The logarithmically averaged estimate of the roughness length for the 17-day period was $2 \times 10^{-3}$ m, which compares favorably with the published values of $z_0$ for fresh snow of $\leq 10^{-3}$ m [Lettman, 1969; McRae et al., 1982]. The arithmetic mean was $10^{-2}$ m, with a variance of $6 \times 10^{-4}$ m$^2$. Our data were insufficient to estimate a displacement height, inclusion of which should give a lower $z_0$ estimate.

Using the individual roughness length estimates for each 15-min interval (recognizing that surface snow conditions at Summit can change significantly from day-to-day), the friction velocity for each interval was computed. The average friction velocity estimate for the 20-day period was 0.35 m sec$^{-1}$ and the variance 0.011 m$^2$ s$^{-2}$.

In rough flow regimes, the laminar sublayer is nonexistent or negligible, while in smooth flow regimes the laminar sublayer is proportional to $\frac{u_*}{u_c}$, where $u_c$ is the kinematic viscosity and is equal to 0.14 cm$^2$ sec$^{-1}$. The conditions for rough and smooth flow regimes have been experimentally determined to be [Seinfeld, 1986]:

$$\frac{u_*z_0}{u_c} < 0.13$$

(3)

$$\frac{u_*z_0}{u_c} > 2.5$$

Using these criteria, the 15-min data were classified into smooth and rough flow regimes. Ninety-seven percent of the samples were classified as rough, while less than 1% were classified as smooth. While our data were insufficient to estimate effects of atmospheric stability, we did the same classification assuming $z_0$ is 10% of those estimated from (1). In that case, 58% were classified as rough, with less than 1% classified as smooth. This analysis suggests that for most of the 17-day interval, there was little or no laminar sublayer present at Summit.

From an analysis of the vertical soundings we also calculated turbulent exchange coefficients for the atmosphere ($K_{zz}$) and used them to calculate concentration profiles in the atmosphere:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z} \left( K_{zz} \frac{\partial C}{\partial z} \right)$$

(4)

Values ranged from less than $10^{-2}$ to 1.0 m$^2$s$^{-1}$ a few meters above the snow and generally increased with height (Figure 5). We calculated vertical profiles of H$_2$O$_2$ for the range of $K_{zz}$ and inversion heights en-
countered using (4). For this analysis we assumed an 
\( \text{H}_2\text{O}_2 \) concentration of 1 ppbv from homogeneous pho-
tochemical sources [Neftel et al., 1995], and a boundary 
condition of 3.6 ppbv at the top of the snowpack. This 
is an assumed boundary condition, based on the gas 
phase \( \text{H}_2\text{O}_2 \) concentration in equilibrium with the sur-
face snow [Conklin et al., 1993]. In three of the profiles, 
days 158, 159, and 160, \( \text{H}_2\text{O}_2 \) rapidly mixed through-
out the atmosphere below the inversion. \( K_{zz} \) values on 
these days were 0.1–1 m\(^2\) s\(^{-1}\) at a height of 4 m, up 
to 5–30 m\(^2\) s\(^{-1}\) at a height of 110 m. Two of these 3 
days had medium inversion heights, while there was no 
inversion on day 160. On days 161 and 165, inversion 
heights were medium and high, respectively, but \( K_{zz} \) 
values were less than 0.3 m\(^2\) s\(^{-1}\) throughout the height 
below the inversion. On these days, the modeled \( \text{H}_2\text{O}_2 \) 
atmospheric profiles failed to reach steady state after 12 
hours of degassing, and the \( \text{H}_2\text{O}_2 \) concentrations in the 
atmosphere were calculated to be well below those at 
the boundary (Figure 6). A second set of profiles was 
calculated using 2.0 ppbv as the boundary condition, 
which gave atmospheric values nearer those reported on 
Figure 1a, and gradients on the order of 0.1 \( \mu \text{g} \text{ m}^{-4} \).

Discussion

The nighttime decrease in atmospheric \( \text{H}_2\text{O}_2 \), which 
followed temperature and humidity (Figures 1 and 3), 
can be explained by cocondensation of water molecules 
and \( \text{H}_2\text{O}_2 \) on the surface snow. Water was being de-
posited at night, and cocondensation of \( \text{H}_2\text{O} \) and \( \text{H}_2\text{O}_2 \) 
occurs. Even if cocondensation was not stoichiometric, 
\( \text{H}_2\text{O}_2 \) would still be removed by codeposition of \( \text{H}_2\text{O}_2 \) 
and \( \text{H}_2\text{O} \) molecules. Release of \( \text{H}_2\text{O}_2 \) did not neces-
sarily follow coevaporation. On some days the morn-
ing increase in atmospheric \( \text{H}_2\text{O}_2 \) followed temperature 
more than specific humidity, suggesting that adsorption 
rather than absorption controlled short-term retention 
of \( \text{H}_2\text{O}_2 \) in the snow. But on other days, especially 
in the 1990 record, it closely follows specific humidity. 
Adsorbed \( \text{H}_2\text{O}_2 \) should desorb in response to a temper-
ature increase, whereas absorbed \( \text{H}_2\text{O}_2 \) should be re-
leased with sublimation of water. It thus appears that 
both processes were important.

The \( \text{H}_2\text{O}_2 \) concentration in surface snow increased 
during the period shown on Figure 1, however. This 
suggests that net uptake was not restricted to a pure ad-
sorption/desorption at the surface, but that uptake/release of the bulk phase was involved. This was apparently the case for laboratory experiments reported previously [Conklin et al., 1993]. Alternatively, the deposition could reflect deposition of diamond dust [clearly shown in Conklin et al., 1993]. Alternatively, the deposition could reflect deposition of diamond dust (clearly shown in Conklin et al., 1993). From this observation it can be inferred that either degassing in the field was kinetically limited, the equilibrium concentration was below that found in laboratory studies, or both. The fact that the concentration in the surface snow increased roughly in parallel with the atmospheric concentration argues against significant degassing. However, additions to the snow at night could well exceed degassing during the day, because of codeposition at night. Because the H$_2$O$_2$ mass in surface snow is so much larger than that in the atmosphere below the inversion layer, degassing could cause a large increase in the atmospheric concentration but no detectable change in surface snow.

It could be speculated that the additional H$_2$O$_2$ originated from snow layers beneath the surface. This seems unlikely in view of the decreasing temperature with increasing depth in the summer snow, and the concentration gradients shown on Figure 4. Laboratory studies have shown that below about $-10^\circ$C, the partitioning of H$_2$O$_2$ from air to snow surfaces increases drastically as temperature decreases [Conklin et al., 1993]. High frequency pressure pumping, known to disrupt the thermal regime in snowpacks [Albert and McGilvary, 1992], enhances ventilation of subsurface snow and could contribute to degassing of H$_2$O$_2$. Pressure pumping was shown to enhance the flux of CO$_2$ from soil, through a seasonal snowpack, to the atmosphere by 18-34% [Massman et al., 1995]; however, our H$_2$O$_2$ fluxes and gradients in snow/firn [Bales et al., 1995] are much lower than CO$_2$ fluxes and gradients in seasonal snowpacks [Sommerfeld et al., 1993].

The variations in daytime H$_2$O$_2$ concentration highs were most likely related to changing air mass origin and the passage of frontal systems. Note that the daily average H$_2$O$_2$ on Figure 1a generally follows that for atmospheric pressure (Figure 1e). Over the entire 40-day sampling period a linear regression of H$_2$O$_2$ concentration versus pressure gave a relatively good fit; the standard error was 0.3965. Ozone concentration, measured with a detector (Dashibi) located in the same canvas laboratory building as the first H$_2$O$_2$ detector, showed a drop from 65 ppbv on days 158-159, to 40 ppbv on days 161-162, and then a small rise in concentration (Figure 1f).

**Conclusions**

Our measurements showed that degassing of H$_2$O$_2$ from the snow surface was slow, and thus may not be a plausible explanation for the measured atmospheric values exceeding those estimated from model calculations. Lower measured versus predicted equilibrium H$_2$O$_2$ concentration just above the snow surface, and lower H$_2$O$_2$ in firn gas [Bales et al., 1995] both indicate that H$_2$O$_2$ is released slowly from the snow, if at all. Because surface snow contains so much more H$_2$O$_2$ than the atmosphere below the atmospheric inversion height, however, even a slow degassing would increase atmospheric concentrations. During the period analyzed, surface snow was accumulating H$_2$O$_2$, even in the absence of snowfall, apparently from cocondensation of H$_2$O and H$_2$O$_2$. Previous studies have reported H$_2$O$_2$ losses in pits sampled over more than 1 year. Our current work suggests that these losses must have occurred later in the summer or fall, after the May-July field season. The cumulative evidence suggests that surface snow adjusts slowly to drops in atmospheric H$_2$O$_2$ concentration, over time scales of at least weeks.
Acknowledgments. This work was supported in part by National Science Foundation grants DPP-9123025 and OPP-9224192 to the University of Arizona and OPP-922296-93 to the University of Wisconsin. M. Bergin collected the fog samples. S. Oltmans (NOAA Climate Monitoring and Diagnostics Laboratory) provided the ozone detector. J. Choi assisted with model calculations. R. Brice did the manuscript preparation.

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