

H₂O₂ in snow, air and open pore space in firn at Summit, Greenland

Roger C. Bales, Mark V. Losleben, Joseph R. McConnell

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

Katrin Fuhrer

Physics Institute, University of Bern, Bern, Switzerland

Albrecht Neftel

Swiss Federal Research Station for Agricultural Chemistry and Hygiene of the Environment, Liebfeld-Bern, Switzerland

Abstract. Measurements of H₂O₂ in firn gas down to a 1.7-m depth showed a consistent trend, with higher firn-gas concentrations generally associated with higher concentrations in the firn at the same depth. However, firn to firn-gas concentration ratios still exhibited a seasonal dependence, suggesting that for summer layers equilibrium has not yet been reached. The time to reach equilibrium between firn and firn gas is at least weeks. Snowfall and fog deposit several times more H₂O₂ than the surface snow will retain at equilibrium, supporting the idea that surface snow is a temporary reservoir for H₂O₂. Thus from an equilibrium standpoint, the snow-pack should be a source of atmospheric H₂O₂ in the summer as well as fall, resulting in higher daytime concentrations than would occur based on just atmospheric photochemical reactions. But firn-gas measurements reported here were generally near or lower than those in the atmosphere, suggesting that degassing is too slow to significantly influence atmospheric H₂O₂ levels.

Introduction

Researchers have attempted to use H₂O₂ records in polar ice cores to infer past trends in atmospheric oxidation capacity, assuming a constant and linear transfer function between H₂O₂ concentrations found in the ice and those in the atmosphere [Thompson, 1995]. However even a qualitative comparison between H₂O₂ records from different locations in Greenland and Antarctica clearly shows that the transfer function is neither constant, nor even a simple linear function of temperature and accumulation differences between sites, and that post-depositional changes on all time scales alter the concentrations [Neftel *et al.*, 1995]. H₂O₂ concentrations in summertime surface snow are consistently higher than those in buried summer layers [*e.g.* Sigg, 1990]. A quantitative understanding of the loss processes is still lacking. In the top few tenths of a me-

ter of snow, and the next 1-2 meters of consolidated, metamorphosed firn, both slow grain-scale mass transfer and slow exchange of air in the open pore space of snow/firn (firn gas) with the atmosphere can limit the rate of H₂O₂ loss from the snow/firn. Conklin *et al.* [1993] took a laboratory approach using simple column experiments to establish a grain-scale, equilibrium transfer function. These investigations resulted in a temperature dependent ratio of C_{ice}/C_{atm} similar to Henry's law, but approximately one percent of actual Henry's coefficient values extrapolated from 25°C to below freezing.

In this paper we report a first attempt to extend gas-phase H₂O₂ measurements into the open pore space of the consolidated snow (firn) that had fallen from 0.5-2.5 years earlier. The purpose of the research was to test the hypothesis that whereas freshly fallen snow is supersaturated with respect to H₂O₂ partitioning between ice and air, in snow/firn that has been buried more than a few weeks, the ice grains and surrounding air reach equilibrium with respect to H₂O₂ phase partitioning.

Methods

These studies were carried out at the Greenland Ice Sheet Project 2 (GISP2) camp at Summit, Greenland in May through July of 1993. We measured H₂O₂ in the air 3 m above the snow, in the firn gas, in surface snow, in snow/firn samples taken from the walls of 2-m deep pits, in fog and in fresh snowfall. Methods for these are described sequentially.

The gas-phase H₂O₂ detector involved drawing air and pumping H₂O₂-free water into a scrubber, where the H₂O₂ was transferred from the air to the water; the H₂O₂ content of the water was then analyzed using a peroxidase method [Sigg *et al.*, 1992]. Our main modification was to use a coil rather than diffusion scrubber, resulting in 100% recovery of H₂O₂ from the air. During most of the sampling period the atmospheric detector system was located in an electrically 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 were estimated

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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 versus without the sampling tube; differences were insignificant.

Firn-gas measurements involved coring a 75 or 100-mm diameter hole with a Cieba tube or hand auger, respectively, to the measurement depth, and withdrawing a firn sample for later analysis. The inlet tube and thermocouple were attached to an epoxy coated rod that placed the thermocouple but not the inlet in direct contact with the firn. The hole was then sealed about 100 mm above the bottom with an inflatable balloon and snow. The depth of the hole sampled was typically about 0.3–1.6 m. A new hole was cored for each sample at a distance greater than the draw-down area from the previous firn-gas sample site. Firn-gas sampling lasted 10 min (1 L min^{-1}) and each depth was repeated, with no significant concentration difference between the two samples. Temperatures were taken at the same time and in the same location as the firn-gas samples. The firn-gas sampling site was in the clean-air sector at the main GISP2 camp, about 100 m in the prevailing up-wind direction from the drilling dome and 400 m from combustion sources.

Line losses due to H₂O condensation occurred during the firn-gas measurements because the probe was moved between the warm atmosphere (-5 to -10°C) and the cold firn (-14 to -22°C). Losses were estimated by sampling outside air before (warm probe) and after (cold probe) making firn-gas measurements, with and without the probe and inlet tubing for 10 min each. The average loss from five tests on three different days was 71 percent, with a range of 67–74 percent. All firn-gas measurements were thus multiplied by 3.4. Several different configurations for the firn-gas inlet system were tested over the two-week period prior to making the first measurement. Although losses for this system were relatively high, they were judged to be sufficiently reproducible.

Surface-snow samples were collected daily at the atmospheric sampling camp, which is 30 km in the prevailing upwind direction from the GISP2 camp. Samples were collected at various times during the day, depending on the availability of personnel. Five replicates were taken from the entire surface snow layer, defined by visual observation of grains and layering. The average depth sampled was 20 mm, with a range of 3–60 mm. The still-frozen samples were brought to the GISP2 camp, melted and generally analyzed within one hour after melting. Analyses were done on an instrument with the same design as used for the atmospheric measurements. Aliquots were refrozen and analyzed back in our laboratory in Tucson three months later, with comparable results (within 2 percent). A 2-m snow pit was dug and sampled at the atmospheric sampling camp on day 158, with sample handling and analysis the same as for surface-snow samples.

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.

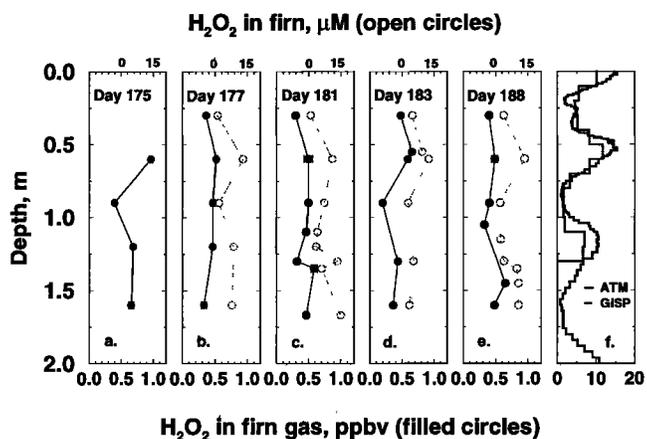


Figure 1. a–e) Firn-gas and firn H₂O₂ concentrations on five different days. Error bars represent uncertainty in accounting for line losses. f) H₂O₂ in snow pit dug at atmospheric sampling camp (ATM) on day 158. The sampling interval was 10 mm in the upper 0.6 m, 20 mm down to 1.2 m, and 40 mm down to 2 m. Less-detailed results from a pit dug at the GISP2 camp on day 145 are shown for comparison.

Fog or snow was allowed to accumulate overnight, and scraped into bottles at about 0630–0730 hours. Sample handling and analysis was as for the surface-snow samples.

Air temperatures were measured at two heights (0.2 and 1.8 m above the snow) at the same site as atmospheric measurements were made. A thermocouple was placed inside a reflective cylinder and values recorded using a data logger (Campbell Scientific). Snow temperatures associated with firn-gas sampling were also taken using a thermocouple and recorded on a data logger.

Results

Figure 1a–e shows the five vertical profiles of the H₂O₂ concentration in the open pore space of the snowpack together with the snow/firn concentrations. H₂O₂ concentrations in firn gas were 0.5–1.0 ppbv. Atmospheric concentrations on those same days averaged slightly higher, 0.4–1.2 ppbv. Relative concentrations between H₂O₂ in firn and open pore space were consistent over the depth sampled; that is, depths with high firn-gas concentration also had the highest firn concentration. Because only spot firn measurements were made in association with firn-gas sampling, results from a 2-m pit shown on Figure 1f were used to more-clearly establish summer versus winter layers. Summer layers are distinguished by high H₂O₂ concentrations and winter layers by low values, reflecting the seasonality of photochemical production. Note that the pits and spot firn samples will not match exactly, because the pit was sampled on day 158 at the atmospheric camp, 30 km from the site of firn-gas sampling. Samples from a shallow pit that was 100 m from the site of firn-gas measurements (Figure 1f) shows a good correspondence between the two locations.

H₂O₂ concentrations in the atmosphere showed a general increase from 0.5 to 2.0 ppbv over the period day

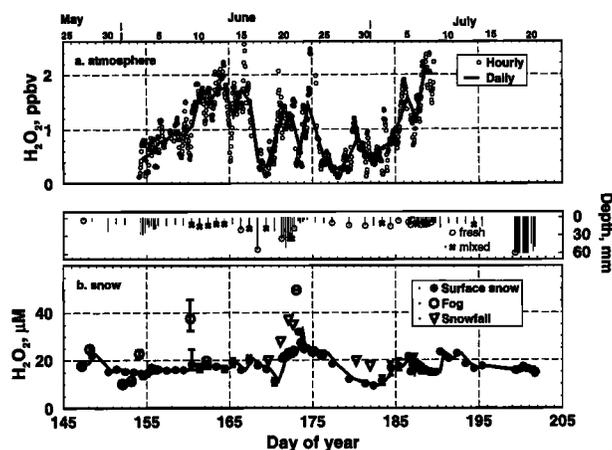


Figure 2. H₂O₂ in the atmosphere and surface snow. a) Average hourly H₂O₂ concentrations measured at GISP2 camp. b) Average and range (error bars) of surface snow samples taken at atmospheric sampling camp. Also shown are fog and fresh snow samples collected in trays at the main GISP2 camp. Upper panel indicates depth of layer sampled, and whether the layer was fresh snow (o) a mixture of fresh and aged snow (x) or entirely aged snow (no symbol).

154-164, during which there was no snowfall (Figure 2a). Concentrations exhibited a diel variation, with daytime highs and nighttime lows that differed by about 0.5 ppbv. This increase was followed by a general decline through day 169, when there was snowfall. During this same day 154-169 period, there was a small increase in H₂O₂ concentration in the surface snow layer (Figure 2b), from about 15 to 18 µM. During most of these days there was evidence of hoar or rime deposition, and a few nights of diamond dust (clear sky precipitation) or fog deposition. For days 150-161, the surface layer consisted of snow that fell on day 150. After that, new snowfall plus wind redistribution resulted in a surface layer that was a mix of snow that fell on day 150 and subsequent snowfalls. Heavy fog deposition was evident in the day 160 surface sample, but no influence was seen in later samples. For days 170-173 there was a general increase in surface snow H₂O₂ concentrations associated with snowfall. On day 173 surface snow reached a season high of about 30 µM; fog collected at the same time had 50 µM H₂O₂. From day 174 through day 182 there was a decline in H₂O₂ in surface snow. Atmospheric concentrations also showed a general decline over most of the same period.

There was low spatial variability in surface snow H₂O₂, on the scale of 1 m (Figure 2b). Depth of the surface snow layer changed from day to day, due to the combined effects of spatial heterogeneity, wind redistribution and snowfall.

Discussion

We can compare the ratios of H₂O₂ concentrations in snow/firn to air to assess the approach to equilibrium of different parts of the firn/snow/air system. In Figure 3 the ratio is plotted as function of depth and corresponding temperature at the time of measurement. Shown

for comparison is the equilibrium partition coefficient (K_D) as determined by Conklin *et al.* [1993] in laboratory studies, and a line representing co-condensation of H₂O and H₂O₂ (i.e. same molar ratio in snow as in atmosphere). The partition coefficient increases strongly with decreasing temperature, as does the co-condensation ratio. Thus colder snow has a greater capacity to take up H₂O₂.

Comparing the firn to firn-gas ratios given in Figure 3a with the firn concentration versus depth on Figure 1f shows that higher ratios generally were found in summer and lower ratios found in winter layers. The respective means of 4.5 and 4.2 M atm⁻¹, are different at the 90% confidence level. Examining the same firn to firn-gas ratios as a function of temperature (at time of measurement) on Figure 3b shows a significant positive deviation from the equilibrium line for nearly all summer values and for some winter values, suggesting that the firn is still supersaturated with respect to the firn gas.

The variability within summer and winter values is expected, because we made diffuse rather than point measurements. Nor were the measurements centered on the summer peak or winter minimum. The volume of air sampled was about 12 times that in the cored hole below the balloon seal. The distance from which air was drawn was on the order of 150 mm, about 1.5-2 times the hole diameter. In homogeneous media on the order of 50-60% of this air would come from the open pore space of firn at the same depths as that of the sealed hole, with the remainder being firn gas from above and below. Because of layering in the firn, however, the horizontal permeability should exceed that in the vertical direction, resulting in more than 50-60% of the air sample coming from the same depth as the sealed hole. Thus each sample represents an integration over a vertical distance of 200-300 mm, with more than half of

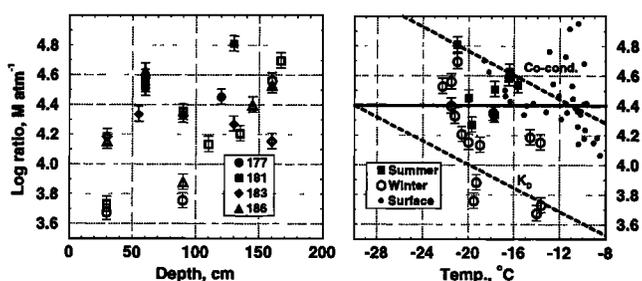


Figure 3. Ratios of snow/firn to firn-gas concentrations (Figure 1). a) Ratios plotted as a function of depth. Open symbols are winter and filled symbols summer layer from profile sampled on day indicated. Error bars represent the range of line-loss estimates for firn-gas measurements. b) The same data are plotted as a function of temperature, distinguishing summer vs. winter layers rather than sampling day. The ratio of H₂O₂ in surface snow to average daily atmospheric H₂O₂ is also shown, plotted versus average daily temperature. The sloping dashed lines for co-condensation and K_D are from Conklin *et al.* [1993]. The horizontal dashed line is the K_D for -30°C, the annual average temperature.

the sample coming from the 100-mm vertical distance of the sealed hole.

We consider three possible explanations for the apparent non-equilibrium between firn and firn gas. First, the firn and the summer snow layers could still reflect in part the initial concentrations established during the formation of the snow, where the transfer is given by co-condensation. The ratios of daily average H_2O_2 in the surface snow to the corresponding atmospheric concentration are also shown on Figure 3b, plotted versus daily average temperature. Though not directly comparable to firn and firn gas ratios because the surface snow should reflect atmospheric concentrations at the time of snowfall, they do indicate the position of the system relative to equilibrium. These values cluster around the co-condensation line, suggesting that H_2O_2 concentrations in surface snow were 4-8 times the laboratory-determined equilibrium value. Changes in this ratio with time were apparently dominated by changes in atmospheric H_2O_2 concentrations.

Second, the system may reflect an equilibrium with colder winter and spring temperatures rather than the warmer summer temperatures. In that case, both the summer and winter points should be compared to the horizontal "annual average" line on Figure 3b. The average winter value falls below this line (-30°C), with the average summer value still above the line. At the grain scale, H_2O_2 at the ice-air interface at each depth may be in equilibrium with H_2O_2 in firn gas, but the bulk-ice H_2O_2 out of equilibrium due to slow degassing of summer layers and slow incorporation in winter layers. The fact that winter minima change little during the first few years after snow is deposited provides further evidence for slow exchange of H_2O_2 between bulk ice and the firn gas.

Third, the losses could be greater than we estimated, with firn-gas concentrations correspondingly higher. This is unlikely given that our line-loss measurements on different days gave consistent values.

Post-depositional changes of H_2O_2 concentrations in snow and firn involve different time scales. In the absence of precipitation, surface snow adapted to changing atmospheric concentrations very little during our field season. The lack of complete equilibrium in the firn-gas profiles suggests that deeper (buried) layers are still adjusting their concentrations to the surrounding gas concentrations over times of several months to years. The time scale for air to move between winter and summer layers (~ 0.3 m), and between buried summer layers and the atmosphere (> 0.6 m) should be on the order of hours to days.

Conclusions

H_2O_2 in buried firn slowly approaches an equilibrium with firn gas, with the rate-limiting step apparently being transport through the solid phase. The co-condensation model implicitly assumes a homogeneous distribution of H_2O_2 in the ice matrix. As the firn approaches equilibrium, the grain-scale distribution of H_2O_2 becomes heterogeneous rather than homogeneous, with the grain surface in summer firn having lower H_2O_2 concentrations than does the grain interior.

The reverse would be true for winter layers. Once on the surface of the ice grain, H_2O_2 will readily exchange with the surrounding air. Conklin *et al.* [1993] estimated the solid diffusion coefficient of H_2O_2 to be of the same order of magnitude as for self-diffusion of H_2O in the ice matrix. This results in equilibration times on the order of weeks to months, depending on the ice grain diameter. Our current results suggest that the equilibration time is at least weeks, and possibly years.

Snowfall and fog deposit several times more H_2O_2 than the surface snow will retain at equilibrium, supporting the idea that surface snow is a temporary reservoir for H_2O_2 . Thus from an equilibrium standpoint the snowpack should be a net source of atmospheric H_2O_2 in the summer as well as fall, resulting in higher daytime concentrations than would occur based on just atmospheric photochemical reactions. But firn-gas measurements reported here were generally near or lower than those in the atmosphere, reinforcing the point that degassing is too slow to significantly influence summer atmospheric H_2O_2 levels.

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R. C. Bales, M. Losleben, J. McConnell, Department of Hydrology and Water Resources, University of Arizona, Tucson, Arizona, USA

Katrin Fuhrer, Physics Institute, University of Bern, Bern, Switzerland

Albrecht Neftel, Swiss Federal Research Station for Agricultural Chemistry and Hygiene of the Environment, Liebfeld-Bern, Switzerland

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