

## Sensitivity of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and formaldehyde (HCHO) preservation in snow to changing environmental conditions: Implications for ice core records

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[1] Sensitivity studies with physically based numerical air–snow–firn transfer models for formaldehyde (HCHO) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) show that even though nonlinear processes determine the preservation of HCHO and H<sub>2</sub>O<sub>2</sub> in snow and firn, changes in atmospheric mixing ratios are linearly recorded in ice cores under otherwise constant environmental conditions. However, temperature, snowpack ventilation, and rate and timing of snow accumulation also affect the ice core records of reversibly deposited species and must be considered when inferring past atmospheric mixing ratios. The results of the sensitivity studies allow quantitative separation of these factors in ice core records. Past temperatures and accumulation rates are generally determined in ice cores and the preservation of HCHO and H<sub>2</sub>O<sub>2</sub> is not highly sensitive to snowpack ventilation, leaving changes in seasonality of snow accumulation as the main source of uncertainty in a reconstruction of past atmospheric mixing ratios. *INDEX TERMS:* 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 1610 Global Change: Atmosphere (0315, 0325); 1827 Hydrology: Glaciology (1863); 1863 Hydrology: Snow and ice (1827); 3344 Meteorology and Atmospheric Dynamics: Paleoclimatology; *KEYWORDS:* air–snow exchange, ice core, formaldehyde, hydrogen peroxide, Greenland, snow

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### 1. Introduction

[2] Records of impurities in ice cores have yielded a wealth of information about Earth's past climate, atmospheric circulation patterns and atmospheric composition [Legrand and Mayewski, 1997]. Lately, chemical analyses on ice cores have been expanded and improved with high-resolution continuous flow analyses (CFA) using fluorescence and absorption spectrometry [Röthlisberger et al., 2000a], with Inductively Coupled Plasma Mass Spectrometry based continuous trace element analyses (CFA-TE) [McConnell et al., 2002] and with fast ion chromatography (FIC) [Udisti et al., 2000; Littot et al., 2002]. Concentrations of a range of impurities (ions, molecules, trace elements, and dust) present in ice can be and are being routinely measured continuously along ice cores with depth resolutions as small as 1 cm.

[3] For many species, a quantitative reconstruction of the chemical ice core records with respect to past atmospheric mixing ratios is not yet possible because of a lack of

understanding of physical and photochemical processes governing the inclusion and preservation of those impurities in snow, firn and ultimately ice. Specifically, so-called reversibly deposited species such as formaldehyde (HCHO), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), carboxylic acids, nitric and hydrochloric acid circulate between the snow and the atmosphere until exchange with the atmosphere is cut off by burial [Hutterli et al., 1999, 2001, 2002; McConnell et al., 1998a; Bales and Choi, 1996; Fuhrer et al., 1996; Röthlisberger et al., 2003; Wagnon et al., 1999].

[4] Not only is the quantitative knowledge of air–snow exchange important for the interpretation of ice core records, it has been shown that due to physical and photochemical processing, the snowpack can be a strong source or sink for a variety of species and so impact the local atmospheric photochemistry [e.g., Dibb et al., 1998; Hutterli et al., 1999, 2001, 2002; Jacobi et al., 2002; Jones et al., 2000; Sumner et al., 2002].

[5] The focus of this work is on H<sub>2</sub>O<sub>2</sub> and HCHO. They show concentration increases of 60% and up to 90%, respectively, in ice core records from Summit over the last 200 years [Anklin and Bales, 1997; Sigg and Neftel, 1991; Staffelbach et al., 1991]. Both are closely linked to the oxidizing capacity of the atmosphere. Air–snow transfer of these species has been extensively investigated in field, laboratory and modeling studies [Sigg et al., 1992; Conklin et al., 1993; Neftel et al., 1995; Bales and Choi, 1996; Fuhrer et al., 1996; McConnell et al., 1997a, 1997b, 1998a;

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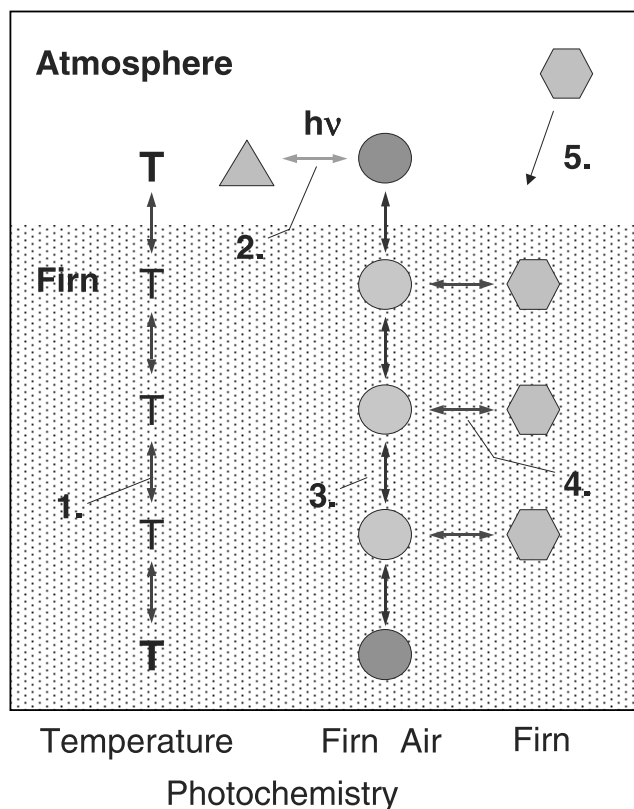
Hutterli *et al.*, 1999, 2001, 2002; Burkhardt *et al.*, 2002]. Physically based numerical air–snow transfer models successfully simulate measured concentration profiles in firn and their evolution in time in a forward way [Hutterli *et al.*, 1999, 2002; McConnell *et al.*, 1998a]. Starting from well-defined and calibrated transfer models for present-day conditions at Summit, Greenland, we investigate the sensitivity of the preservation of HCHO and H<sub>2</sub>O<sub>2</sub> in firn and ice to environmental changes. We develop a quantitative tool for both the inversion of chemical ice core records to past atmospheric mixing ratios and for the prediction of the impact of climate change on air–snow interactions in the future. An important aspect of the study is to identify the sources and magnitudes of uncertainties inherent in the inversion of ice core records. The approach avoids the need to actually solve the underlying inverse problem defined by the coupled, nonlinear partial differential equations governing the air–snow transfer.

## 2. Air–Snow–Firn Transfer Models

[6] The numerical, time-dependent, one-dimensional (1-D) HCHO and H<sub>2</sub>O<sub>2</sub> air–snow–firn transfer models used in this study have been described previously [Hutterli *et al.*, 2001, 2002; McConnell *et al.*, 1998a]. Here only a summary is given focusing on recent model improvements while the model parameters specific for the sensitivity studies are described in detail. Present-day Summit, Greenland conditions (72.6°N, 38.5°W, 3200 m elevation, −32°C annual mean temperature, 23 g cm<sup>−2</sup> yr<sup>−1</sup> accumulation uniformly distributed) were used for the baseline runs to make the results directly applicable to existing firn and ice core records from this site. Moreover, most previous air–snow transfer field studies have been conducted at Summit and the models have been tested and validated extensively for this site. Further, temperatures are close to those used in laboratory studies to determine physical uptake/release parameters on ice surfaces, effectively minimizing uncertainties inherent in extrapolating published values to other temperature regimes.

[7] Five main processes are simulated in the transfer models: heat transfer, gas-phase photochemistry, gas-phase diffusion, air–ice uptake/release, and snow accumulation (Figure 1). At each time step, three profiles are calculated in the snowpack: firn temperatures, firn air mixing ratios, and concentrations in the ice phase. For firn temperatures, measurements from automatic weather stations are used as boundary values. For firn air mixing ratios, gas-phase diffusion within the porous firn and exchange with the atmospheric boundary layer are considered, along with reversible temperature-driven uptake and release by the ice phase. Either measured atmospheric mixing ratios or predicted values based on gas-phase photochemical modeling or both can be used for the mixing ratios in the boundary layer.

[8] To allow direct comparison of the relative sensitivities of HCHO and H<sub>2</sub>O<sub>2</sub> preservation in firn to environmental changes, the same air and firn temperatures were used in both models. The latter were calculated according to the study of Hutterli *et al.* [1999] based on a density profile measured at Summit in 1999. The same density profile was used to calculate specific surface area [Narita, 1971] and to determine effective grain size radii used in the H<sub>2</sub>O<sub>2</sub> transfer model. Air temperatures were from the GISP2 automatic



**Figure 1.** Concept of the 1-D air–snow–firn transfer models. The shapes symbolize individual boxes of the three calculated profiles (T: temperature, circles: gas-phase mixing ratio, hexagons: snow-phase concentration) and the atmospheric composition needed for atmospheric photochemistry calculations (triangle). The boundary values (top) and boundary conditions (bottom) are indicated by dark shapes. The arrows stand for the transfer processes considered: (1) Heat transfer, (2) Gas-phase photochemistry, (3) Gas-phase diffusion, (4) Air–ice uptake/release, and (5) Accumulation.

weather station at Summit (<http://uwamrc.ssec.wisc.edu/aws/awsproj.html>). Vertical mixing coefficients in the firn air are based on molecular diffusivities and corrected for temperature and firn densities according to the study of Schwander [1989]. Background atmospheric mixing ratios were calculated with the NASA Goddard Space Flight Center interactive box model for Summit conditions [Stewart *et al.*, 1983; Hutterli *et al.*, 2001]. As it was not feasible to directly couple the photochemical model with the transfer models, the calculated annual HCHO and H<sub>2</sub>O<sub>2</sub> cycles were scaled to fit observed values [Hutterli *et al.*, 1999, 2001], implicitly accounting for the feedback between the snowpack emissions and the boundary layer composition. Resulting summertime and wintertime values are on the order of 1360 and 0.5 pptv, respectively, for H<sub>2</sub>O<sub>2</sub> and 350 and 120 pptv for HCHO. The relatively short atmospheric lifetimes due to photochemical and physical removal limit the impact of transport on the atmospheric mixing ratios at Summit. An exception is wintertime HCHO (photochemical lifetime of several months compared to a few hours in summer), which could be elevated due to long-range transport. This is to some extent taken into account with the scaling. It is

important to note that the resulting model sensitivities do not significantly depend on the actual values of atmospheric mixing ratios or the exact form of the annual cycles used in the baseline run. However, as discussed below, changes in both level and form of the annual cycle affect the snow profiles.

[9] Temperature-driven air–ice uptake/release is formulated differently in the HCHO and H<sub>2</sub>O<sub>2</sub> transfer models. Based on indications that surface processes are important in the air–ice exchange of HCHO [Staffelbach, 1990; Couch *et al.*, 2000; Jacobi *et al.*, 2002], adsorption and desorption kinetics are simulated in the HCHO transfer model assuming a linear adsorption isotherm [Hutterli *et al.*, 1999]. In the case of the H<sub>2</sub>O<sub>2</sub> transfer model, the air–ice exchange is determined by solid state diffusion within the bulk of the ice crystals [McConnell *et al.*, 1998a; Hutterli *et al.*, 2001]. In reality, surface and bulk processes will take place for both species. However, both approaches lead to qualitatively the same temperature dependence of the uptake/release rates and both approaches are based on empirically determined, Henry's Law type air–ice equilibrium partitioning [Conklin *et al.*, 1993; McConnell *et al.*, 1997c; Hutterli *et al.*, 1999; Burkhart *et al.*, 2002] Thus, the temperature-dependent uptake/release of HCHO and H<sub>2</sub>O<sub>2</sub> in the models should be considered empirical relationships that include adsorption, bulk diffusion, and desorption.

[10] In both models, fresh snow can be added at any time step, resulting in an advection of the snow into deeper layers. During this process, the density of a snow layer moving into deeper depth increases while the specific surface area decreases and the effective grain size increases. Thus, the impact of the morphological evolution of the snow (recrystallization) on the air–snow exchange is taken into account in the models. In order to prevent numerical diffusion in this process, the box heights in the models decrease with depth so that the mass of snow in each layer is the same.

[11] For the HCHO model a top box height of 1 cm was chosen, resulting in a depth resolution of 1 cm or less in the top 2.3 m. Below that, the box height was increased by 2.6% relative to the overlying box. This way a depth of about 20 m was reached, at which simple boundary conditions exist (no temperature and HCHO gradients) [Hutterli *et al.*, 1999], while confining the model size to 400 boxes. HCHO concentrations in fresh snow were calculated based on the air–ice equilibrium partitioning defined by the air temperature and atmospheric HCHO mixing ratio at the time of precipitation. The fresh snow concentrations were then scaled by a constant factor  $F$  to reflect the observed super saturation of fresh snow on the ground. The latter is assumed to be mainly due to cocondensation taking place during snow formation [Hutterli *et al.*, 2002]. However, colder temperatures at cloud level, riming and higher specific surface area of fresh snow compared to aged snow would also contribute to a supersaturation.  $F$  is the only parameter adjusted during the calibration of the model for a specific site. It is optimized for the model to reproduce the HCHO level measured at deeper depth and is unequivocally constrained by the latter. Note that the form and temporal evolution of the simulated HCHO profiles result directly from the physical processes and are not fitted. The vertical resolution of the H<sub>2</sub>O<sub>2</sub> model is 2 cm or less. H<sub>2</sub>O<sub>2</sub>

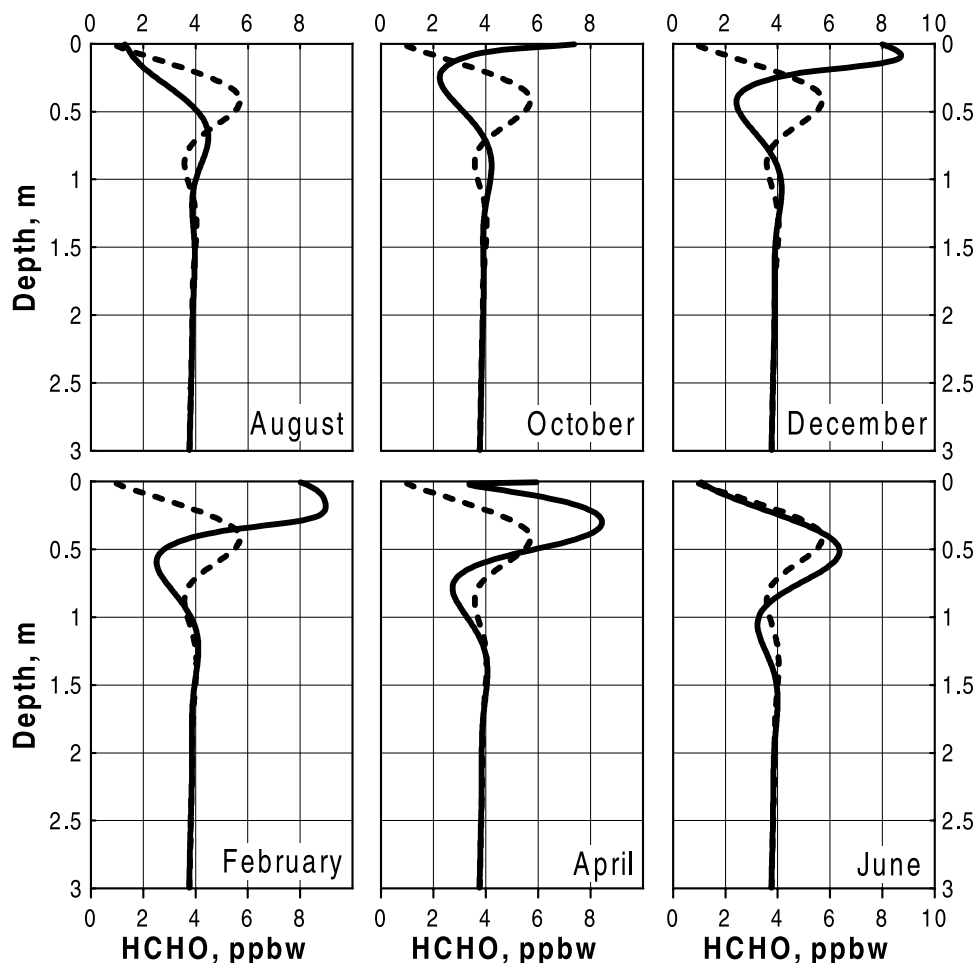
concentrations in fresh snow were calculated based on cocondensation at temperatures measured at ground level, leading to the observed supersaturation of fresh snow with respect to air–snow equilibrium partitioning [McConnell *et al.*, 1998a].

[12] The base for all the sensitivity studies are the HCHO and H<sub>2</sub>O<sub>2</sub> baseline runs respectively, reflecting present-day conditions at Summit. A uniformly distributed accumulation of 23 g cm<sup>-2</sup> yr<sup>-1</sup> was assumed [Steffen and Box, 2001]. For the sensitivity studies, selected model parameters were changed and the impact on the HCHO and H<sub>2</sub>O<sub>2</sub> concentrations in the firm determined. All model runs consisted of 6-year simulations. The HCHO simulations were additionally iterated twice before the actual run, while using the resulting HCHO firm profile as initial values in the subsequent simulation. This assured that the results did not depend on the initial firm profile. The HCHO and H<sub>2</sub>O<sub>2</sub> concentration in the snow layers corresponding to the third year were then averaged and compared to the baseline runs.

### 3. Model Results

[13] The HCHO concentrations in the upper meter of firm change considerably over the course of a year (Figure 2). The simulation of 1 year starting June 1995 is shown, for which simplified model conditions and the observed unusually high accumulation rate for that year were used (1 year of 34.5 g cm<sup>-2</sup> yr<sup>-1</sup> accumulation with a constant fresh snow concentration of 8 ppbw and a constant atmospheric mixing ratio of 0.23 ppbv following a 12-year period with an accumulation rate of 23 g cm<sup>-2</sup> yr<sup>-1</sup> at 10 ppbw) [Hutterli *et al.*, 1999]. Note that of all the HCHO deposited with fresh snow, less than half is preserved. The remainder is released and mixed into the atmosphere during the warm part of the year when near-surface snow temperatures are high and the ice–air equilibrium partition coefficient accordingly low. A fraction of the HCHO released into the firm air by the near-surface snow in summer diffuses into deeper layers where it is taken up by the colder firm at about 1 m depth, filling in the last summer's HCHO trough. Interestingly, the opposite happens in winter, when the near-surface snow is colder than the underlying snow layers: the uptake of HCHO by the cold near surface snow layers in winter leads to snow concentrations in excess of the 8 ppbw deposited. While some of this excess HCHO comes from the overlying atmosphere, most of it diffused from warmer snow layers below 1 m depth up to the colder near-surface layers. Thus, sorption processes lead to a redistribution of volatile species in the firm through the gas-phase opposite to temperature gradients.

[14] In Figure 3, the effect of different levels of the annual temperature cycle on the evolution of HCHO profiles in the firm is shown for the period from 1994.5 to 1998.0. While a constant and uniformly distributed accumulation rate throughout the year was assumed in the simulations, the fresh snow concentrations were calculated based on the modeled atmospheric mixing ratios and measured temperatures adjusted by adding a constant difference between -10°C and +2°C. The variability of the HCHO concentrations in near-surface snow is much higher in winter than in summer due to the slower equilibration at colder temper-



**Figure 2.** Modeled HCHO concentration profiles in the course of a year with an accumulation of 90 cm of snow (8 ppbw) and constant atmospheric mixing ratio (see text). The broken line is the June profile for the average annual accumulation (60 cm of snow at 10 ppbw) and represents the initial profile. The elevated concentration at the surface in the April profile is due to fresh snow deposition shortly before.

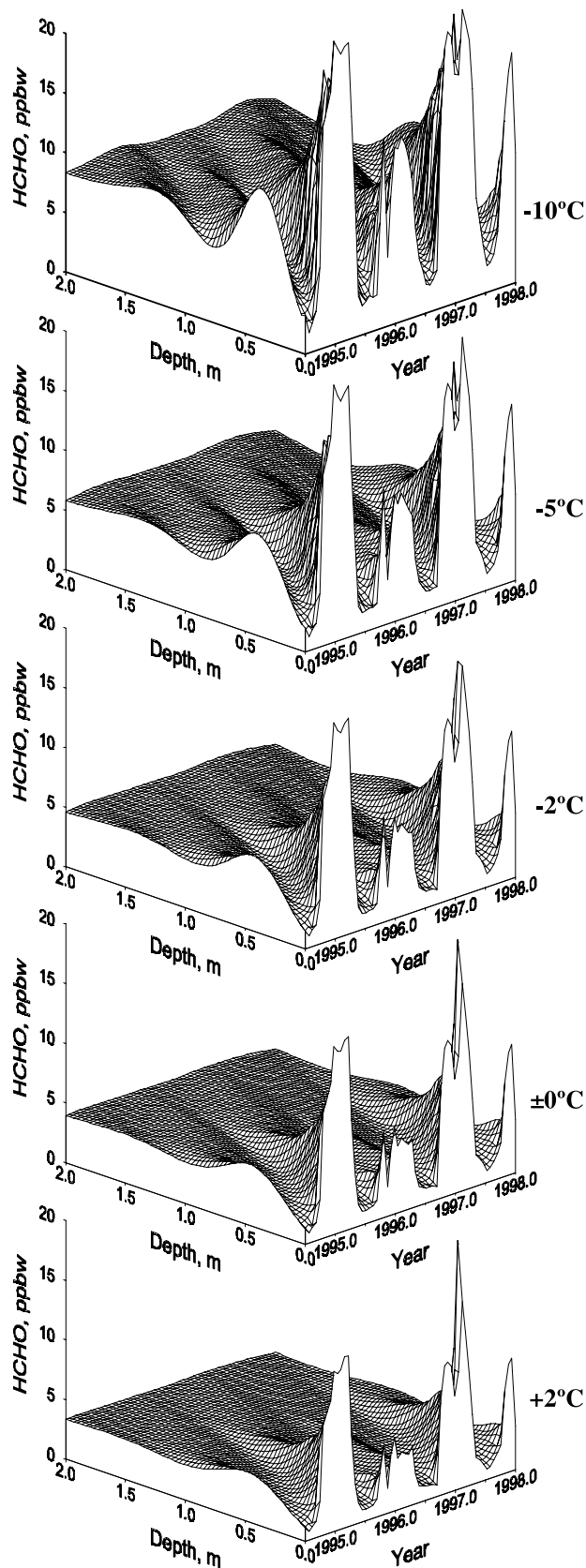
atures. For the same reason, annual cycles are preserved longer at the colder temperatures. Also note that even though the same accumulation rate was used, the annual HCHO cycle is confined to a smaller depth interval in colder snowpacks due to the lower mobility of the HCHO molecules in the firn. Extraordinarily warm temperatures in winter 1995–1996 led to lower modeled HCHO concentrations in the fresh snow. However, in reality the high temperatures were accompanied by a 50% increase in annual snow accumulation, compensating for much of the temperature effect (Figure 2).

[15] In Figure 4, modeled and measured H<sub>2</sub>O<sub>2</sub> profiles at Summit are compared. The model simulation is based on a succession of years with the same annual and diurnal cycles of air temperatures and modeled atmospheric mixing ratios and using a uniform accumulation distribution of 23 g cm<sup>-2</sup> yr<sup>-1</sup>. It is in very good agreement with the profile of a 1998 pit sampled at Summit close to an accumulation stake which showed a uniform accumulation distribution throughout the preceding year [McConnell *et al.*, 1998b]. To visualize the magnitude of the postdepositional changes in the snow, the initial concentrations of the snow layers at the time of deposition are also plotted. Clearly, most of the H<sub>2</sub>O<sub>2</sub>

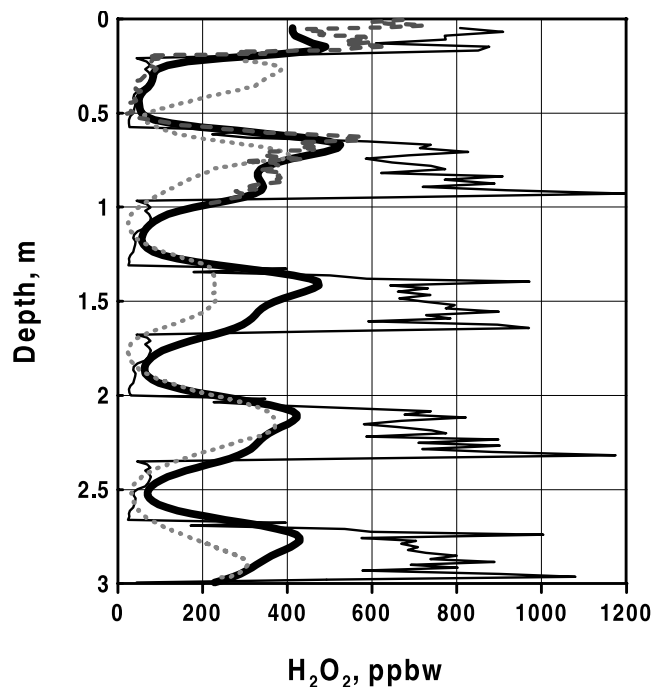
release to the atmosphere takes place in the first year after burial and especially in the near surface snow layers during summer when the temperatures are highest and the snow is most super saturated. In deeper layers, peaks drop and troughs fill in slowly because of the redistribution by diffusion through the firn air. Also shown in Figure 4 is a H<sub>2</sub>O<sub>2</sub> profile from a firn core drilled in 1999 6 km SSE of the Summit camp (to facilitate comparison with the model run it was shifted down by 0.2 m to compensate for the low 1998–1999 winter accumulation). The measured profile also demonstrates the variability in H<sub>2</sub>O<sub>2</sub> profiles associated to a large degree with the interannual variability of the accumulation and the temperature cycle.

[16] Figure 5 depicts the relative changes of HCHO and H<sub>2</sub>O<sub>2</sub> concentrations preserved in the firn with respect to the baseline runs. Figure 5a shows that atmospheric HCHO and H<sub>2</sub>O<sub>2</sub> mixing ratios are linearly recorded in polar snow, if all other variables remain unchanged. However, it is also important to note that the linearity is only warranted when the whole annual cycle of atmospheric mixing ratios is scaled. Due to the highly nonlinear processes involved, even at constant annual average atmospheric mixing ratios, preserved concentrations in snow will change when the





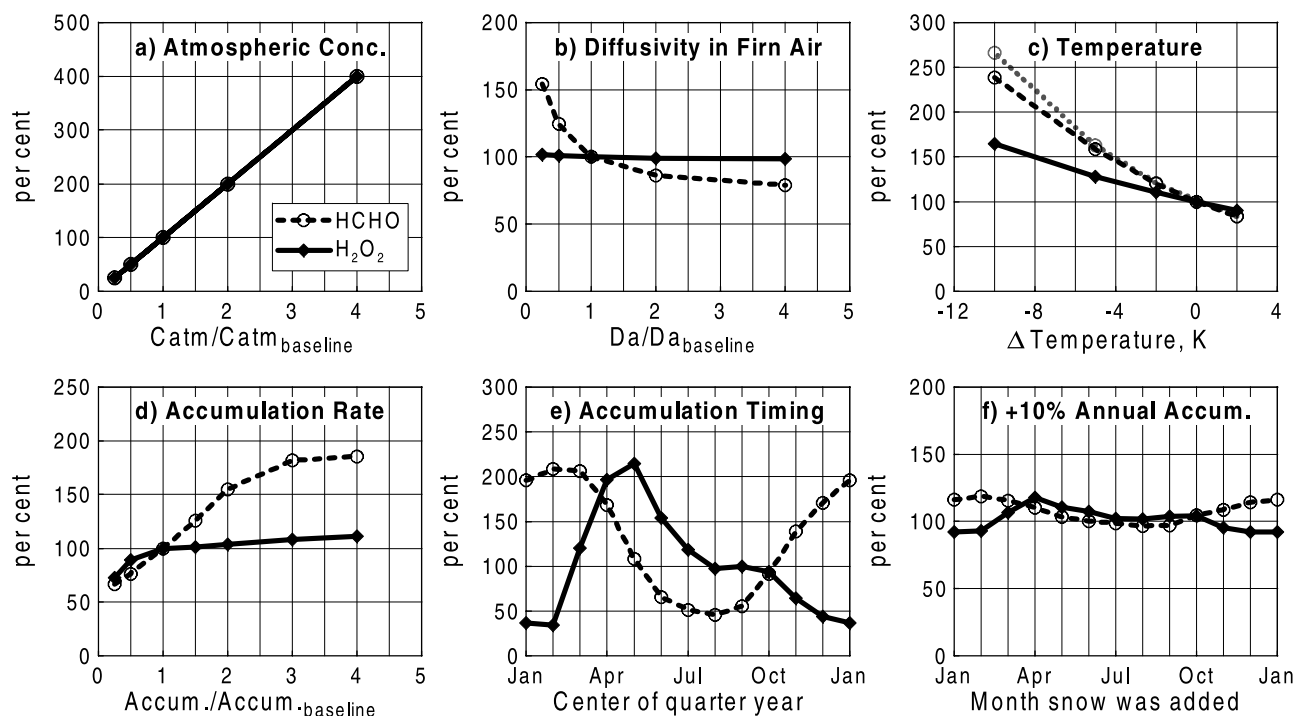
**Figure 3.** Temporal evolution of the HCHO concentration profiles and temperature dependence of HCHO preservation in firm.



**Figure 4.** Modeled H<sub>2</sub>O<sub>2</sub> concentration profile with a uniform accumulation distribution and constant annual cycles of temperature and atmospheric mixing ratios (thick solid line). The fine solid line represents the concentrations of the corresponding snow layers at the time of deposition. The dashed line is a profile measured at Summit in summer 1998 close to an accumulation stake that recorded a uniform accumulation distribution during the preceding year [McConnell *et al.*, 1998b]. The dotted line is a H<sub>2</sub>O<sub>2</sub> profile measured at Summit in summer 1999 (to facilitate comparison, it has been shifted downward by 0.2 m).

seasonality is changing, that is, winter values are increasing, while summer values are decreasing.

[17] While changes in snowpack ventilation (i.e., vertical mixing) has virtually no effect on the preservation of H<sub>2</sub>O<sub>2</sub> under current Summit conditions, the more volatile species HCHO appears to be quite sensitive (Figure 5b). As a lower limit, vertical mixing (i.e., effective diffusivities in firm air) is determined by molecular diffusion scaled down to account for the porosity of the firm [Schwander *et al.*, 1997]. Such values were used in the baseline run because forced ventilation induced by wind blowing over sastrugis is not expected to significantly increase the vertical mixing of HCHO in the snowpack at Summit: the characteristic time for a HCHO molecule to diffuse across the top box (1 cm) in the model is  $\sim 1$  s, about 5 times faster than by forced ventilation in the top centimeters of the snowpack at Siple Dome, Antarctica ( $\sim 0.2$  cm s<sup>-1</sup>) [Albert, 2003] at wind speeds similar to the annual average at Summit (4.1 m s<sup>-1</sup>) [Steffen and Box, 2001]. Using the diffusivity of 0.3 m<sup>2</sup> s<sup>-1</sup> reported for forced ventilation in the top centimeters of a snowpack at Alert, Canada, at a wind speed of 9 m s<sup>-1</sup> [Albert and Schultz, 2002] and taking into account the strong attenuation of forced ventilation with depth ( $e$ -folding depth  $\sim 0.3$  m) [Albert, 2003], the estimated average total effective diffusivity of HCHO in the top 0.5 m at



**Figure 5.** Sensitivities to changing environmental conditions of preserved HCHO and H<sub>2</sub>O<sub>2</sub> in firn relative to the baseline run (current Summit conditions: 100%). (a) The annual cycle of atmospheric concentrations is scaled by a constant factor, (b) the diffusivity  $D_a$  in firn air, which depends on the porosity of the firn and forced ventilation, is scaled, (c) constant values are added to the measured air temperatures (dotted gray curve represents results using the laboratory-determined air–ice partition coefficient; see text), (d) the annual accumulation rate is scaled, (e) the whole baseline annual accumulation is deposited homogeneously within 3 consecutive months, and (f) An additional 10% of the annual accumulation is deposited in 1 month.

Summit is less than twice the molecular diffusivity. Thus, a doubling of the annual mean wind speed at Summit would decrease the HCHO preservation by less than 15%.

[18] Because of higher uptake capacity of ice and the slower equilibration rates, more HCHO and H<sub>2</sub>O<sub>2</sub> is preserved at colder temperatures (Figure 5c). Using the recently published laboratory-determined effective sorption parameters for HCHO on pure ice [Burkhart *et al.*, 2002] instead of the parameters determined in Summit snow [Hutterli *et al.*, 1999], the model is slightly more sensitive to temperature changes. The difference between the two sets of sorption parameters are thought to be mainly due to the snow not having reached complete equilibrium with the air during the experiments with actual values lying somewhere in between. Part of the difference might also be due to impurities in present-day snow at Summit, which could potentially affect the partitioning characteristics of HCHO.

[19] Lower accumulation rates lead to lower preservation (Figure 5d). Below a critical accumulation rate, near-surface snow has enough time to fully equilibrate with the atmosphere at the annual atmospheric mixing ratio and temperature. However, on timescales below 1 year, snow equilibration is always lagging changes in atmospheric mixing ratios. With increasing accumulation rate, surface snow is buried by subsequent precipitation, impeding contact with the atmosphere and leading to an incomplete

equilibration and ultimately preservation out of the atmosphere–ice equilibrium relative to the mean annual temperature. However, note that the atmosphere–firn equilibration nevertheless reaches steady state and changes in atmospheric mixing ratios are still linearly reflected in the deeper firn layers. While annual HCHO signals in the firn are smoothed out within a couple of years, they are preserved far longer in the H<sub>2</sub>O<sub>2</sub> profiles (depending on the accumulation rate from tens of years to centuries). For both species, a plateau of the annual average concentrations preserved in the firn is reached with high accumulation rates. This is due to the surface snow being buried by subsequent precipitation before it can significantly exchange with the atmosphere, leading to preservation of virtually all HCHO and H<sub>2</sub>O<sub>2</sub> originally deposited. For H<sub>2</sub>O<sub>2</sub> the highest sensitivity to accumulation rate is below  $12 \text{ g cm}^{-2} \text{ yr}^{-1}$ , while for HCHO it is between 20 and  $40 \text{ g cm}^{-2} \text{ yr}^{-1}$ . It is important to note that the sensitivity values are specific for current Summit conditions and would be different for significantly colder or warmer conditions. However, the effect of the accumulation rate on the preservation is also apparent in the different levels of H<sub>2</sub>O<sub>2</sub> in records from ice cores drilled relatively nearby each other in Dronning Maud Land, East Antarctica [Sommer *et al.*, 2000] and for HCHO in pits in the vicinity of South Pole Station [Hutterli *et al.*, 2002].

[20] The mean accumulation rate is generally higher at a site with higher annual mean temperature [e.g., Lorius *et al.*,

1985], leading to a combination of the curves in Figures 5c and 5d when comparing records from different sites. Thus, starting at high accumulation (temperature) sites, the temperature effect is expected to dominate. However, at very low accumulation, the long exposure to the atmosphere will lead to lower preserved levels of HCHO and H<sub>2</sub>O<sub>2</sub>, even though average temperatures are colder. It is interesting to note that this behavior has been observed for nitrate in Antarctic and Greenland ice cores [Röthlisberger *et al.*, 2000b, 2007].

[21] There is a strong impact of the annual distribution of accumulation on the preservation of HCHO and H<sub>2</sub>O<sub>2</sub>. In Figure 5e, the results of model runs in which the annual snow accumulation was deposited during a 3-month period are shown. The model results reveal different responses of HCHO and H<sub>2</sub>O<sub>2</sub>. They are due to the interplay of the annual cycles of atmospheric mixing ratios and temperature. The virtually zero winter H<sub>2</sub>O<sub>2</sub> mixing ratios cause below average fresh snow concentrations, even though temperature is low as well. In spring H<sub>2</sub>O<sub>2</sub> mixing ratios are increasing and temperatures are still low, leading to the highest H<sub>2</sub>O<sub>2</sub> fresh snow concentrations at that season. The annual cycle of atmospheric mixing ratios dominates the H<sub>2</sub>O<sub>2</sub> fresh snow concentrations. In the case of HCHO, however, the annual temperature cycle is dominating over the atmospheric mixing ratios, leading to more HCHO preserved with winter precipitation only and less than normal with summer precipitation only. This leads to the opposite signs of the impact of accumulation timing on the preservation of HCHO and H<sub>2</sub>O<sub>2</sub> throughout much of the year.

[22] The model runs shown in Figure 5e represent upper limits for potential impacts of changes in annual accumulation distribution. In Figure 5f, a more realistic scenario with respect to the variability of multiyear average accumulation distribution was investigated. An additional 10% of the average annual accumulation was deposited during 1 month of the year. Based simply on this increased annual accumulation rate and the results in Figure 5c, one would expect higher HCHO and H<sub>2</sub>O<sub>2</sub> levels. While this is on average true, it is not for additional precipitation in summer and winter for HCHO and H<sub>2</sub>O<sub>2</sub>, respectively. The latter cases cause a dilution of the annual HCHO and H<sub>2</sub>O<sub>2</sub> concentrations in the snow for the same reasons as discussed in the previous paragraph.

[23] There is evidence of unknown heterogeneous photochemical reactions producing HCHO in snow [Sumner *et al.*, 2002]. Results from experiments where the snowpack was alternately shaded and unshaded, however, indicate that such a production could increase near-surface firn air mixing ratios only by less than 15% at South Pole (M. A. Hutterli *et al.*, Formaldehyde and hydrogen peroxide in air, snow and interstitial air at South Pole, submitted to *Atmospheric Environment*, 2002) in summer, when a production is expected to be highest. This is consistent with similar measurements at Summit (H.-W. Jacobi, personal communication, 2002). In both experiments, no consistent H<sub>2</sub>O<sub>2</sub> changes were detected in the firn air. Snow chamber experiments with fresh snow from Michigan did not reveal evidence of a light-induced HCHO production [Couch *et al.*, 2000]. While the results presented are not affected by a presence of such a production, past changes in the latter

would also be reflected in the preservation of HCHO. Model results show that a 15% increase in the summertime firn air mixing ratios caused by an additional HCHO source in the near-surface snow layers leads to an increase of less than 15% in HCHO preservation. The impact of past changes of such a source on ice core records should thus be well below 15%.

[24] As a potent oxidant, H<sub>2</sub>O<sub>2</sub> is not conserved in ice containing relatively high amounts of impurities. At Summit it decays to about half within 5000 years. It limits the length of a possible reconstruction of atmospheric mixing ratios and requires an additional correction of  $\sim 1\%$  century<sup>-1</sup> of the mean H<sub>2</sub>O<sub>2</sub> concentrations [Sigg and Nefel, 1991; Fuhrer *et al.*, 1993]. This effect, however, is much smaller in the cleaner Antarctic ice, where H<sub>2</sub>O<sub>2</sub> is preserved for more than 15,000 years [Nefiel and Fuhrer, 1993]. There is no clear evidence for a HCHO decay in ice cores.

#### 4. Conclusions

[25] The impacts of changing atmospheric composition, temperature, accumulation distribution, and snowpack ventilation on the preservation of HCHO and H<sub>2</sub>O<sub>2</sub> in snow and firn have been quantified. While the approach is general, the results are specific to HCHO and H<sub>2</sub>O<sub>2</sub> for current Summit environmental conditions. However, because the sensitivities do not vary much over a range of several degrees Celsius and between  $\sim 80\%$  and  $\sim 150\%$  of the current accumulation rate at Summit, the results are also applicable to Holocene ice core records from other areas on the Greenland and Antarctic ice sheets. For the same reason, uncertainties in the values used in the baseline run do not have a significant effect on the calculated sensitivities. Qualitatively, the results are representative also for other species with temperature dependencies of air–ice partitioning and annual cycles of atmospheric mixing ratios similar to those of HCHO or H<sub>2</sub>O<sub>2</sub>. Caution is called for with ice core records containing melt layers, as the latter can be associated with a severe redistribution of soluble species and impeded vertical mixing of the air in the firn.

[26] The model results show that even though nonlinear physical processes determine the preservation of HCHO and H<sub>2</sub>O<sub>2</sub> in snow and firn, atmospheric mixing ratios are linearly recorded in ice cores under otherwise unchanged environmental conditions. However, temperature, ventilation, the rate and timing of accumulation and (photo-)chemistry in the snow and ice also affect the ice core records of reversibly deposited species and need to be considered when inferring past atmospheric mixing ratios. The impact of a heterogeneous HCHO production in snow is likely small, as is the chemical decay of H<sub>2</sub>O<sub>2</sub>. Past temperatures and accumulation rates can be deduced for a specific ice core from the  $\delta^{18}\text{O}$  record and annual layer thickness measurements based on high-resolution CFA data, respectively. However, changes in timing of accumulation and in the snowpack ventilation are not readily available. The latter only plays a minor role for HCHO and can be neglected for H<sub>2</sub>O<sub>2</sub>, but changes in the timing of accumulation are critical and represent the biggest remaining obstacle in the quantitative inversion of HCHO, H<sub>2</sub>O<sub>2</sub> and possibly other ice core records. High-resolution multiproxy CFA records from high accumulation sites offer the poten-



tial to help constrain shifts in annual accumulation distribution in the past. Such high-resolution records allow determination of the relative timing of subannual markers such as annual maximum and minimum concentrations in the various species. However, relative shifts can be caused by both a change in subannual accumulation distribution and by changes in the annual cycle of the source strength and transport patterns. To disentangle those processes and so constrain past changes in accumulation timing will require a multiproxy approach taking advantage of the different responses of the various species as seen in Figure 5e. Note that deposition of irreversibly deposited species is also affected by the timing of accumulation and so can be used to constrain the latter: Apart from the relative timing of minima and maxima, their levels also depend on whether snow accumulated during the time of atmospheric minimum or maximum concentration.

[27] The temporal resolution of a reconstruction of atmospheric mixing ratios is determined by the accumulation rate and the characteristic distance the species diffused in the firn and ice by the time it is measured. At Summit, this is on the order of several years for H<sub>2</sub>O<sub>2</sub> and a few decades for HCHO when pore close-off is reached, after which their mobility is governed by the much slower solid state diffusion.

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## References

- Albert, M. R., Effects of snow and firn ventilation on sublimation rates, *Ann. Glaciol.*, in press, 2003.
- Albert, M. R., and E. F. Schultz, Snow and firn properties and air-snow transport processes at Summit, Greenland, *Atmos. Environ.*, **36**, 2789–2797, 2002.
- Anklin, M., and R. C. Bales, Recent increase in H<sub>2</sub>O<sub>2</sub> concentration at Summit, Greenland, *J. Geophys. Res.*, **102**, 19,099–19,104, 1997.
- Bales, R., and J. Choi, Conceptual framework for interpretation of exchange processes, in *Chemical Exchange Between the Atmosphere and Polar Snow*, NATO ASI Ser., vol. 43, edited by E. W. Wolff and R. C. Bales, pp. 319–338, Springer-Verlag, New York, 1996.
- Burkhardt, J. F., M. A. Hutterli, and R. C. Bales, Partitioning of formaldehyde between air and ice at –35°C to –5°C, *Atmos. Environ.*, **36**, 2157–2163, 2002.
- Conklin, M. H., A. Sigg, A. Neftel, and R. C. Bales, Atmosphere-snow transfer function for H<sub>2</sub>O<sub>2</sub>: Microphysical considerations, *J. Geophys. Res.*, **98**, 18,367–18,376, 1993.
- Couch, T. L., A. L. Sumner, T. M. Dassau, P. B. Shepson, and R. E. Honrath, An investigation of the interaction of carbonyl compounds with the snowpack, *Geophys. Res. Lett.*, **27**, 2241–2244, 2000.
- Dibb, J. E., R. W. Talbot, J. W. Munger, and D. J. Jacob, Air-snow exchange of HNO<sub>3</sub> and NO<sub>y</sub> at Summit, Greenland, *J. Geophys. Res.*, **103**, 3475–3486, 1998.
- Fuhrer, K., A. Neftel, M. Anklin, and V. Maggi, Continuous measurements of hydrogen peroxide, formaldehyde, calcium and ammonium concentrations along the new GRIP ice core from Summit, Central Greenland, *Atmos. Environ.*, **27**, 873–880, 1993.
- Fuhrer, K., M. Hutterli, and J. McConnell, Overview of recent field experiments for the study of the air-snow transfer of H<sub>2</sub>O<sub>2</sub> and HCHO, in *Chemical Exchange Between the Atmosphere and Polar Snow*, NATO ASI Ser., vol. 43, edited by E. W. Wolff and R. C. Bales, pp. 307–318, Springer-Verlag, New York, 1996.
- Hutterli, M. A., R. C. Bales, and R. Röthlisberger, Atmosphere-to-snow-to-firn transfer studies of HCHO at Summit, Greenland, *Geophys. Res. Lett.*, **26**, 1691–1694, 1999.
- Hutterli, M. A., J. R. McConnell, R. W. Stewart, H.-W. Jacobi, and R. C. Bales, Impact of temperature-driven cycling of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) between air and snow on the planetary boundary layer, *J. Geophys. Res.*, **106**, 15,395–15,404, 2001.
- Hutterli, M. A., R. C. Bales, J. R. McConnell, and R. W. Stewart, HCHO in Antarctic snow: Preservation in ice cores and air-snow exchange, *Geophys. Res. Lett.*, **29**, 10.1029/2001GL014256, 2002.
- Jacobi, H.-W., M. M. Frey, M. A. Hutterli, R. C. Bales, O. Schrems, N. J. Cullen, K. Steffen, and C. Koehler, Measurements of hydrogen peroxide and formaldehyde exchange between the atmosphere and surface snow at Summit, Greenland, *Atmos. Environ.*, **36**, 2619–2628, 2002.
- Jones, A. E., R. Weller, and E. W. Wolff, Speciation and rate of photochemical NO and NO<sub>2</sub> production in Antarctic snow, *Geophys. Res. Lett.*, **27**, 345–348, 2000.
- Legrand, M., and P. Mayewski, Glaciochemistry of polar ice cores: A review, *Rev. Geophys.*, **35**, 219–243, 1997.
- Littot, G. C., Comparison of analytical methods used for measuring major ions in the EPICA Dome C (Antarctica) ice core, *Ann. Glaciol.*, in press, 2003.
- Lorius, C., C. Ritz, L. Merlivat, N. I. Barkov, Y. S. Korotkevich, and V. M. Kotlyakov, A 150,000-year climatic record from Antarctic ice, *Nature*, **316**, 591–596, 1985.
- McConnell, J. R., R. C. Bales, J. R. Winterle, H. Kuhns, and C. R. Stearns, A lumped parameter model for the atmosphere-to-snow transfer function for hydrogen peroxide, *J. Geophys. Res.*, **102**, 26,809–26,818, 1997a.
- McConnell, J. R., R. C. Bales, and D. R. Davis, Recent intra-annual snow accumulation at South Pole: Implications for ice core interpretation, *J. Geophys. Res.*, **102**, 21,947–21,954, 1997b.
- McConnell, J. R., J. R. Winterle, R. C. Bales, A. M. Thompson, and R. W. Stewart, Physically based inversion of surface snow concentrations of H<sub>2</sub>O<sub>2</sub> to atmospheric concentrations at South Pole, *Geophys. Res. Lett.*, **24**, 441–444, 1997c.
- McConnell, J. R., R. C. Bales, R. W. Stewart, A. M. Thompson, M. R. Albert, and R. Ramos, Physically based modeling of atmosphere-to-snow-to-firn transfer of H<sub>2</sub>O<sub>2</sub> at South Pole, *J. Geophys. Res.*, **103**, 10,561–10,570, 1998a.
- McConnell, J. R., R. C. Bales, and J. F. Burkhardt, Year-round surface snow measurements as a proxy for atmospheric H<sub>2</sub>O<sub>2</sub> at Summit, Greenland, *Eos Trans. AGU*, **79**(45), F298, 1998b.
- McConnell, J. R., G. W. Lamorey, S. W. Lambert, and K. C. Taylor, Continuous ice-core chemical analyses using inductively coupled plasma mass spectrometry, *Environ. Sci. Technol.*, **36**, 7–11, 2002.
- Narita, H., Specific surface of deposited snow II, *Low Temp. Sci.*, **A29**, 69–81, 1971.
- Neftel, A., and K. Fuhrer, A record of atmospheric oxidant from polar ice cores over the past 100,000 years: Dream or real possibility?, in *The Tropospheric Chemistry of Ozone in the Polar Region*, NATO ASI Ser., vol. 17, edited by H. Niki and K. H. Becker, pp. 219–233, Springer-Verlag, New York, 1993.
- Neftel, A., R. C. Bales, and D. J. Jacob, H<sub>2</sub>O<sub>2</sub> and HCHO in polar snow and their relation to atmospheric chemistry, in *Ice Core Studies of Global Biogeochemical Cycles*, NATO ASI Ser., vol. 130, edited by R. J. Delmas, pp. 249–264, Springer-Verlag, New York, 1995.
- Röthlisberger, R., M. Bigler, M. A. Hutterli, S. Sommer, H. G. Junghans, and D. Wagenbach, Technique for continuous high-resolution analysis of trace substances in firn and ice cores, *Environ. Sci. Technol.*, **34**, 338–342, 2000a.
- Röthlisberger, R., E. W. Wolff, R. Mulvaney, M. A. Hutterli, and S. Sommer, Factors controlling nitrate in ice cores: Evidence from the Dome C deep ice core, *J. Geophys. Res.*, **105**, 20,565–20,572, 2000b.
- Röthlisberger, R., et al., Nitrate in Greenland and Antarctic ice cores: A detailed description of post-depositional processes, *Ann. Glaciol.*, **35**, in press, 2003.
- Schwander, J., The transformation of Snow to ice and the occlusion of gases, in *The Environmental Record in Glaciers and Ice Sheets*, edited by C. Langway and O. H. Dahlem Konferenzen, pp. 53–67, John Wiley, New York, 1989.
- Schwander, J., T. Sowers, J.-M. Barnola, T. Blunier, and A. Fuchs, Age scale of the air in the summit ice: Implications for glacial-interglacial temperature change, *J. Geophys. Res.*, **102**, 19,483–19,493, 1997.
- Sigg, A., and A. Neftel, Evidence for a 50% increase in H<sub>2</sub>O<sub>2</sub> over the past 200 years from a Greenland ice core, *Nature*, **351**, 557–559, 1991.
- Sigg, A., T. Staffelbach, and A. Neftel, Gas phase measurements of hydrogen peroxide in Greenland and their meaning for the interpretation of H<sub>2</sub>O<sub>2</sub> records in ice cores, *J. Atmos. Chem.*, **14**, 223–232, 1992.
- Sommer, S., et al., Glacio-chemical study spanning the past 2 kyr on three ice cores from Dronning Maud Land, Antarctica, 1, Annually resolved accumulation rates, *J. Geophys. Res.*, **105**, 411–422, 2000.
- Staffelbach, T., Formaldehyd- und Ammonium-Messungen an Schnee-, Firn- und Eisproben aus polaren und alpinen Regionen, Ph.D. thesis, Phys. Inst., Univ. of Bern, Bern, Switzerland, 1990.



- Staffelbach, T., A. Neftel, B. Stauffer, and D. Jacob, A record of the atmospheric methane sink from formaldehyde in polar ice cores, *Nature*, 349, 603–605, 1991.
- Steffen, K., and J. Box, Surface climatology of the Greenland icesheet: Greenland Climate Network 1995–1999, *J. Geophys. Res.*, 106, 33,951–33,964, 2001.
- Stewart, R. W., S. Hameed, and G. Matloff, A model study of the effects of intermittent loss on odd nitrogen concentrations in the lower troposphere, *J. Geophys. Res.*, 88, 10,697–10,707, 1983.
- Sumner, A. L., et al., Atmospheric chemistry of formaldehyde in the Arctic troposphere at Polar Sunrise, the influence of the snowpack, *Atmos. Environ.*, 36, 2553–2562, 2002.
- Udisti, R., S. Becagli, E. Castellano, R. Mulvaney, J. Schwander, S. Torcini, and E. Wolff, Holocene electrical and chemical measurements from the EPICA-Dome C ice core, *Ann. Glaciol.*, 30, 20–26, 2000.
- Wagnon, P., R. J. Delmas, and M. Legrand, Loss of volatile acid species from upper firn layers at Vostok, Antarctica, *J. Geophys. Res.*, 104, 3423–3431, 1999.
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