

## Analyses of firn gas samples from Dronning Maud Land, Antarctica: Study of nonmethane hydrocarbons and methyl chloride

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[1] Firn air was sampled on the Antarctic plateau in Dronning Maud Land (DML), during the Norwegian Antarctic Research Expedition (NARE) 2000/2001. In this paper, we describe the analyses for methyl chloride and nonmethane hydrocarbons (NMHCs) in these firn air samples. For the first time, the NMHCs ethane, propane, and acetylene have been measured in Antarctic firn air, and concentration profiles for these gases have been derived. A one-dimensional numerical firn air diffusion model was used to interpret the measured profiles and to derive atmospheric concentrations as a function of time. The atmospheric trends we derived for the NMHC and methyl chloride at DML cover the period from 1975 to 2000. Methyl chloride shows a decreasing trend of  $1.2 \pm 0.6$  ppt per year (annual mean concentration  $548 \pm 32$  ppt). For ethane we found an increasing trend of  $1.6 \pm 0.6$  ppt per year (annual mean concentration  $241 \pm 12$  ppt). The concentrations of propane and acetylene appear to be constant over the period 1975–2000, with annual mean concentrations of  $30 \pm 4$  ppt for propane and  $24 \pm 2$  ppt for acetylene. *INDEX*

*TERMS:* 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; *KEYWORDS:* firn air, NMH and methylchloride, atmospheric trends

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### 1. Introduction

[2] Chemical analyses of air trapped in firn allow the reconstruction of the concentrations of atmospheric trace gases. Such a record can go back beyond the earliest direct measurements and can be obtained for remote locations [Schwander *et al.*, 1993; Butler *et al.*, 1999].

[3] This paper focuses on nonmethane hydrocarbons (NMHC) and methyl chloride. These gases play an important role in tropospheric chemistry on regional and global scales. The nonmethane hydrocarbons in this paper, ethane, propane and acetylene, react strongly with OH radicals, which are a major oxidizing agent of the atmosphere. Furthermore, NMHC are responsible for the formation of tropospheric ozone, which is a hazardous gas for the biosphere and acts as a greenhouse gas [Sillman *et al.*, 1995].

[4] Methyl chloride is less reactive with OH radicals, but makes an important contribution to organic chlorine in the

stratosphere [Khalil and Rasmussen, 1999]. This gas, which is emitted by biomass burning and natural sources, contributed approximately 15% of the total stratospheric organic chlorine in 1992 [Montzka *et al.*, 1996]. Because of the emission reduction of anthropogenic halocarbons such as chlorofluorocarbons (CFCs), the relative importance of methyl chloride as a stratospheric chlorine source is slowly increasing [Khalil and Rasmussen, 1999]. In spite of numerous studies of the large-scale distribution of NMHC and methyl chloride, little is still known about their global trends [Clarkson *et al.*, 1997; Khalil and Rasmussen, 1999].

[5] Biomass burning, natural emissions, and use of fossil fuels are the main sources of NMHC and methyl chloride in the atmosphere. The influence of biomass burning and use of fossil fuels can be estimated in Antarctica by use of methyl chloride and ethane, because the relatively long atmospheric lifetimes ( $\tau$ ) of methyl chloride ( $\tau = 1.5$  years) [Keene, 1999] and ethane ( $\tau = 92$  days) [Boissard *et al.*, 1996] permits long-range transport from anthropogenic sources to remote regions. Oceans contribute approximately 10% to the atmospheric NMHC concentrations [Clarkson *et al.*, 1997] and significantly to the methyl chloride concentration [Keene, 1999]. This makes the oceans an important source of these gases, and for Antarctica the only local source. Background levels for propane and acetylene are therefore relatively undisturbed by local events in Antarctica.

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[6] Firn air analyses on NMHCs are presented for the first time in this paper, yielding the longest atmospheric record for ethane, propane and acetylene over Antarctica. The atmospheric seasonal cycle for the NMHCs and methyl chloride are obtained in an accompanying paper by K. A. Kaspers et al. (Analyses of firn gas samples from Dronning Maud Land, Antarctica: Derived seasonal variations of NMHCs and methyl chloride from firn air of the upper layer, submitted to *Journal of Geophysical Research*, 2003).

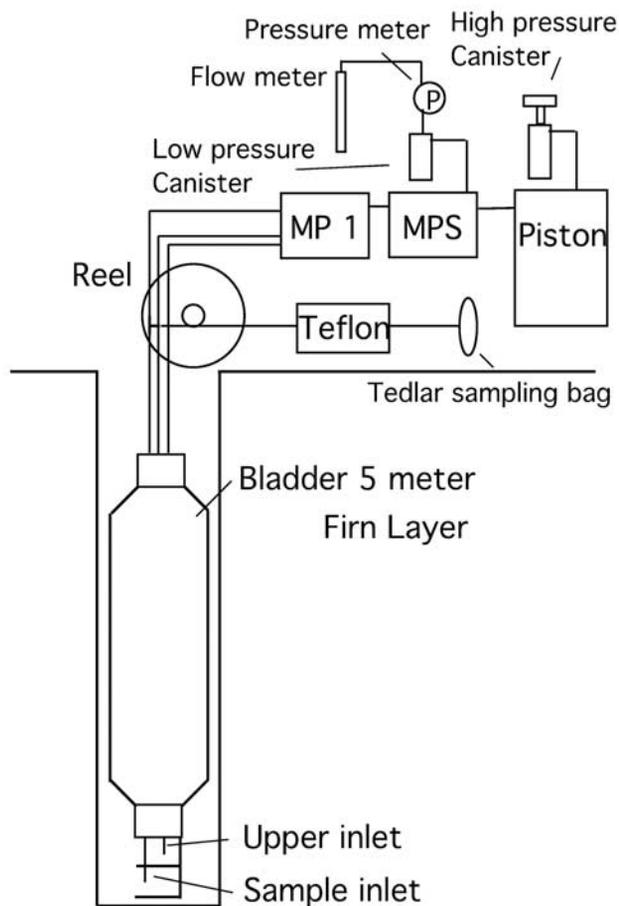
[7] We sampled firn air at a remote location on the Antarctic plateau in Dronning Maud Land (DML) during the NARE 2000/2001 expedition [Winther et al., 2002]. We analyzed the observed concentration profiles and used a one-dimensional numerical firn diffusion model to explain the measured concentration profiles. In the section on the diffusion model we describe the method to obtain time series of concentrations at the surface from the analyzed gases, including an error estimate. This methodology is applied to obtain atmospheric records for methyl chloride, ethane, propane and acetylene over the period 1975–2000.

## 2. Sampling and Analyses

[8] Firn air samples were collected at site M (75.00°S, 15.00°E, 3453 m a.s.l.) in DML during the NARE 2000/2001 expedition [Winther et al., 2002]. Because of the low annual temperature ( $-51^{\circ}\text{C}$ ) and accumulation ( $5.0\text{ cm w.eq. a}^{-1}$ ) at this site [Van den Broeke et al., 1999; Karlöf et al., Accumulation variability in a 8 by 8-km area, eastern Dronning Maud Land, Antarctica, as determined from shallow firn cores and snow pits: Some implications for ice core analysis, submitted to *Journal of Glaciology*, 2003], pore close-off (depth where the air is trapped in air bubbles) is located at a depth of 101 m (C. M. Hofstede et al., Firn accumulation records for the past 1000 years on the basis of dielectric profiling of six cores from Dronning Maud Land, Antarctica, submitted to *Journal of Glaciology*, 2003) (hereinafter referred to as C. M. Hofstede et al., submitted manuscript, 2003).

[9] Samples were collected with a firn air pumping system [Bräunlich et al., 2001] (Figure 1) every 8 m until pore close-off. After 8 m of drilling, the drill was removed and a 5-m-long inflatable rubber bladder was inserted to seal the borehole. Two 100-m-long 3/8-inch perfluoroalkoxy alkane (PFA) tubes went through the bladder and connected the bottom of the borehole with the pumping system at the surface. One of the tubes was used to pump firn air into the bladder at a flow rate of  $0.4\text{ L s}^{-1}$ . The other tube ended 10 cm lower, beneath an aluminum plate, and was used to sample the firn air at a flow rate of approximately  $0.2\text{ L s}^{-1}$ .

[10] At the surface, the sample line was split into more PFA lines. The air was pumped directly into 5-L Tedlar sampling bags via a Teflon membrane pump (KNF Neuberger N840.3 FT.18). Pre-cleaned electropolished stainless steel canisters of 1.5 L, filled with pure nitrogen in order to prevent contamination during transport, were used to sample firn air through a Parker two-stage metal bellow pump at a pressure of 2 bar. The metal pump was also used to pump the extracted firn air into a three-stage, oil-free, modified RIXSA 3 piston compressor [Mak and Brenninkmeijer, 1994]. This compressor was used to fill high-volume air samples to  $\sim 120$  bars in 5-L aluminum cylinders (Scott



**Figure 1.** Firn pumping system. The membrane pump (MP1) was used to fill the bladder with firn air. For sampling the 1.5-L low-pressure canisters (electropolished stainless steel), the two-stage metal bellow pump (MPS) was used to fill the canisters up to 2 bars. The Teflon pump sampled 5-L Tedlar sampling bags (no metal parts). The piston compressor was used for sampling high-pressure containers up to 120 bars.

Marrin). All the samples were taken separately; the high-pressure samples were collected last.

[11] Before sampling, we measured the difference in  $\text{CO}_2$  concentration of the firn air and surface air with a Licor Li6262 analyzer. The surface air was sampled approximately 10 m upwind from the drill tent via a 15-m-long 1/4-inch PFA tube, in order to prevent contamination by generators. We started the collection of samples when the  $\text{CO}_2$  content of the firn air had stabilized.

[12] The air in the stainless steel canisters was analyzed by gas chromatography (GC) for  $\text{CO}_2$ , NMHCs, chlorocarbons, CFCs, and aromatic compounds (see Scheeren et al. [2002] for details). A flame ionization detector (FID) was used for NMHCs and aromatic compounds, and an electron capture detector (ECD) for chlorocarbons (including  $\text{CH}_3\text{Cl}$ ) and CFCs. The precision of the analyses ( $1\sigma$ ) was 2% for CFC-12 and methyl chloride and 5% for the NMHCs. The detection limits for these gases are 15 ppt.

[13] The Centre for Isotopic Research of the University of Groningen measured  $\text{CO}_2$  concentrations in the low-pressure samples (GC; Hewlett-Packard model 6890), expressed

**Table 1.** Scale Factors for Diffusion Coefficients  $D_{12}$  of Gases Relative to the Diffusion Coefficient for  $\text{CO}_2$ <sup>a</sup>

| Molecule                                   | Scaling Factor  |
|--|-----------------|
| $\text{CO}_2$                              | $\equiv 1.00$   |
| CFC-12 ( $\text{CCl}_2\text{F}_2$ )        | $0.61 \pm 0.05$ |
| Methyl chloride ( $\text{CH}_3\text{Cl}$ ) | $0.83 \pm 0.06$ |
| Ethane ( $\text{C}_2\text{H}_6$ )          | $0.93 \pm 0.06$ |
| Propane ( $\text{C}_3\text{H}_8$ )         | $0.73 \pm 0.05$ |
| Acetylene ( $\text{C}_2\text{H}_2$ )       | $1.03 \pm 0.07$ |

<sup>a</sup>According to *Perry and Chilton* [1973].

on the WMO mole fraction scale and on the NOAA CMDL scale.  $\text{CO}_2$  and  $\text{CH}_4$  were separated on a 4-foot-long Haysep Q column. Methane was measured directly by FID.  $\text{CO}_2$  was first converted into methane by a methanizer (nickel catalyst with hydrogen) and then measured on the same FID. The instrument's precision,  $1\sigma$ , for  $\text{CO}_2$  was 0.1% [*Ramonet et al.*, 2002].

[14] Aromatic compounds such as benzene and toluene were measured from the low-pressure firn air samples to determine the amount of contamination. The values for the aromatic compounds were all around or below the detection limit (15 ppt for benzene and toluene) and we therefore concluded that none of the samples had been significantly contaminated.

### 3. Diffusion Model

#### 3.1. Model Description

[15] *Schwander et al.* [1993] introduced the basic equations for gas diffusion in the open channels of the firn layer in terms of the gas flux  $J_{(z,t)}$  (where  $z$  is the depth in the firn layer and  $t$  time, equation (1)). From this equation the concentration  $C_{(z,t)}$  in the firn layer can be determined.

$$J_{(z,t)} = J_{\text{Molecular diffusion}} + J_{\text{Gravity}} = -D_{(z)} \left( \frac{\partial C_{(z,t)}}{\partial z} + \frac{MgC_{(z,t)}}{RT} \right) \quad (1)$$

Here,  $D_{(z)}$  is the total diffusion coefficient,  $R$  the gas constant,  $g$  the gravitational constant,  $T$  the temperature in K at 10 m, and  $M$  the molecular mass (g/mol). The first term between the brackets represents the diffusion resulting from a concentration gradient and the second term the effect of gravity. The diffusion coefficient ( $D_{(z)}$ ) is based on the following equations:

$$D_{(z)} = \frac{D_{12}D_{m(z)}}{1 + 0.5(1 - \pi_{\text{open}(z)})\gamma_{(z)}} \quad (2a)$$

$$D_{m(z)} = D_{T_0, P_0} \frac{P_0}{P_{(z)}} \left( \frac{T}{T_0} \right)^{1.85} \quad (2b)$$

$$P_{(z)} = P_{\text{atm}} \cdot \exp \frac{M_{\text{air}}gz}{RT} \quad (2c)$$

The total diffusion coefficient  $D_{(z)}$  is a function of the species characteristic diffusion coefficient  $D_{12}$ , the diffusion coefficient for standard temperature and pressure  $D_{m(z)}$  [*Schwander et al.*, 1993; *Spahni et al.*, 2003; *Fabre et al.*, 2000], the open porosity profile  $\pi_{\text{open}(z)}$  and the tortuosity function  $\gamma_{(z)}$  (equation (3)). The diffusion coefficient  $D_{m(z)}$  is expressed in equation 2b by  $D_{T_0, P_0}$  as the standard diffusion coefficient ( $12.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ;  $T_0 = 253 \text{ K}$ ,  $P_0 =$

1013 hPa),  $P_{(z)}$  is the pressure as function of depth, annual surface pressure ( $P_{\text{atm}}$ ).

[16] The species-characteristic diffusion coefficients,  $D_{12}$ , for the measured gases are given in Table 1. These values were calculated using the method of *Wilke and Lee* [1955] and *Perry and Chilton* [1973]. Accuracies given in Table 1 are based on *Perry and Chilton* [1973].

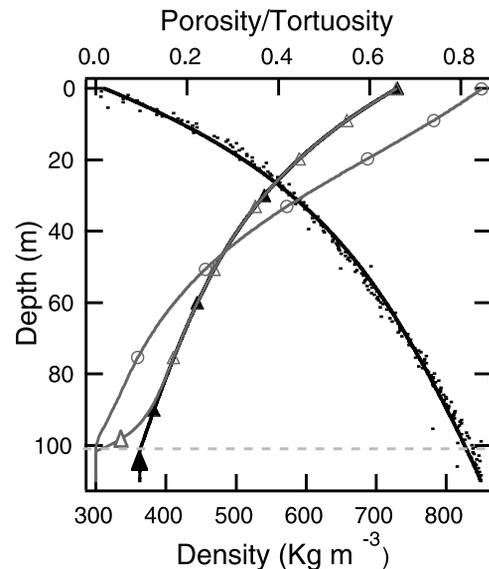
[17] The tortuosity follows from

$$\gamma_{(z)} = \gamma_a + (1 - \gamma_a)(\pi_{\text{Open}(z)})^{-\gamma_b} \quad (3)$$

The tortuosity function ( $\gamma_{(z)}$ ) represents the three-dimensional pore structure of the firn and is used to optimize the diffusion model. Calibrating of the model yields values for  $\gamma_a$  and  $\gamma_b$  (*J. Schwander*, personal communications, 2001).

[18] The open porosity is determined from a semi empirical relation of *Schwander* [1989]. With this relation, the porosity can be calculated from the density profile. The density profile itself is obtained by a polynomial fit through the measured density, which is determined by weighing the ice and by dielectrical profiler measurements (*C. M. Hofstede et al.*, submitted manuscript, 2003). The resulting porosity and tortuosity profiles are shown in Figure 2, together with the measured density profile.

[19] The lower boundary condition to solve equation (1) is that  $\partial C_{(z,t)}/\partial z$  is constant. The upper boundary condition is the surface concentration as a function of time. The latter is the main output parameter of the model and was found iteratively by comparing measured and modeled concentration profiles for the different gases. The firn column was divided into 300 boxes, each containing the same amount of air, so that the firn density and porosity determine the size of the boxes. The model was calibrated with South Pole  $\text{CO}_2$



**Figure 2.** Measured density profile, indicated with dots, and the third-degree polynomial fit. Density was measured in a field lab at Site M [*Winther et al.*, 2002]. The porosity profile indicated by black triangles (including the open porosity, open triangles) was extracted from the empirical relations by *Schwander* [1989]. The tortuosity profile (open circles) was obtained from the open porosity as indicated in equation (3). The horizontal dotted line indicates the pore close-off depth.

ice core data [Siegenthaler *et al.*, 1988] and NOAA-CMDL South Pole data (1976 to present) to simulate the measured CO<sub>2</sub> concentration profile (Figure 3). The model result yields a mean age of  $28 \pm 3$  years at pore close-off for CO<sub>2</sub>. This result was obtained with values for  $\gamma_a$  and  $\gamma_b$  being 0.98 and 3.2.

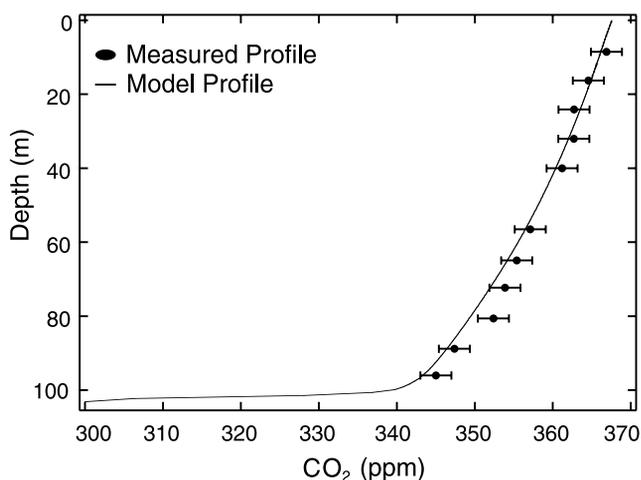
### 3.2. Obtaining Time Series

[20] The model we have used is a numerical model for diffusion in the forward mode, creating a concentration profile. We used the known CO<sub>2</sub> atmospheric history, to calibrate the diffusion model for our specific site (Site M). After we calibrated the diffusion model, an inverse method was used to obtain time series at the surface from the measured concentration profile. Here we describe the inverse method that is able to give an error estimate based on the  $1\sigma$  precision of the measured concentration profile. We describe the inverse method based on CFC-12 measurements (Figure 4). CFC-12 is only emitted by anthropogenic sources [Butler *et al.*, 1999], its lifetime in the atmosphere is 105 years and the gas is chemically inert. Therefore CFC-12 is a very useful gas to test the inverse method. First we adopt an optimal function that best describes the concentration history of CFC-12.

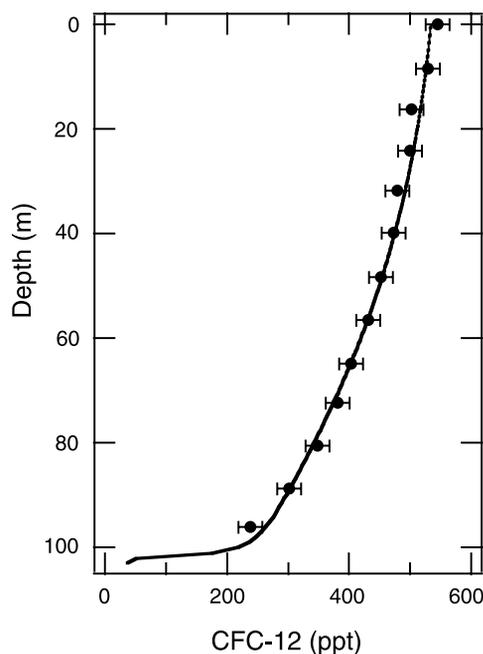
[21] CFC-12 appeared in the atmosphere in the early 1950s. The use and emission strongly increased over the years, until the recognition of its harmful effects on the environment. Emission regulations were agreed upon in the Montreal protocol of 1989, resulting in strongly reduced emissions and a stabilisation of the atmospheric concentration [Prinn *et al.*, 2000]. We assume that the history of CFC-12 can be described by a Gaussian function:

$$C_{\text{CFC-12},(0,t)} = \alpha \cdot e^{-(\beta(t-\chi))^2} \quad (4)$$

$C_{\text{CFC-12},(0,t)}$  is the concentration of CFC-12 in the atmosphere over Dronning Maud Land as a function of time ( $t$  in years). The constants  $\alpha$ ,  $\beta$  and  $\chi$  were derived from an iterative process using the model in forward mode. The



**Figure 3.** Concentration profile of CO<sub>2</sub>. The data set of the measured data is plotted against depth (m) for Site M. The model result was obtained after tuning the tortuosity parameters to fit the measured CO<sub>2</sub> profile. South Pole NOAA Atmospheric CO<sub>2</sub> by Siegenthaler *et al.* [1988] and NOAA-CMDL data were used to force the diffusion model.



**Figure 4.** Concentration profile for the anthropogenic gas CFC-12 (CCl<sub>2</sub>F<sub>2</sub>). The solid line is the best fit through the GC data calculated from the model using a Gaussian time series (Table 2).

model performance was evaluated with a least squares method, such that the difference between modelled and observed CFC-12 profile was minimized. All model results within the  $1\sigma$  precision of the measured concentration profile were accepted as solutions for the CFC-12 atmospheric history. Taking the error in the diffusion coefficient into account (Table 1), we were able to derive an upper and lower limit for the derived time series (Figure 5 and Table 2). There is a good agreement with the directly measured data of Prinn *et al.* [2000] (Figure 5). Our results are furthermore in line with the firn air analyses in DML and at Dome Concordia by Sturges *et al.* [2001] analyses from Law Dome by Sturrock *et al.* [2002] and analyses from Butler *et al.* [1999].

[22] Here, we have indicated that the inverse modeling method yields good results to extract the atmospheric history of a gas over DML from firn air.

[23] Of course, one could argue that we should use other functions than the Gaussian functions. Tests do, however, show no significant improvements. In the next section, we use linear time series for ethane, propane, acetylene and methyl chloride (instead of Gaussian functions). Such functions are more appropriate because previous studies from direct measurements by Khalil and Rasmussen [1999] and Clarkson *et al.* [1997] indicate a linear history for NMHC and methyl chloride in the Southern Hemisphere. No maximum is to be expected like that of CFC-12, whose nonlinear history is the product of its anthropogenic origin and emission regulations.

### 4. Nonmethane Hydrocarbons and Methyl Chloride Analyses in Firn Air

[24] The concentration profiles for methyl chloride, ethane, propane and acetylene represent the period from

**Table 2.** Constants  $\alpha$ ,  $\beta$  and  $\chi$  for the Anthropogenic Gas CFC-12, for a Gaussian Fit<sup>a</sup>

| CFC-12 (CF <sub>2</sub> Cl <sub>2</sub> ) | Function Constants |                                |                |
|---|--------------------|--------------------------------|----------------|
|   | $\alpha$ , ppt     | $\beta$ , ppt yr <sup>-1</sup> | $\chi$ , years |
| Upper limit                               | 538                | $-1.2 \times 10^{-3}$          | 2              |
| Best fit                                  | 536                | $-1.6 \times 10^{-3}$          | 1              |
| Lower limit                               | 530                | $-2.0 \times 10^{-3}$          | 3              |

<sup>a</sup>These constants are derived using the method of the least squares through the measured concentration profile of Figure 4. Uncertainties in the measured profiles and scaling factors (Table 1) for the molecules are incorporated in these values.

1975 to 2000 deduced from model age at pore close-off depth (Figure 6). All gases show a strong decrease in concentration toward the surface in the top 20 m of the firn layer. This part of the firn air is influenced by seasonal variations in gas mixing ratios at the surface and seasonal variations in meteorological parameters.

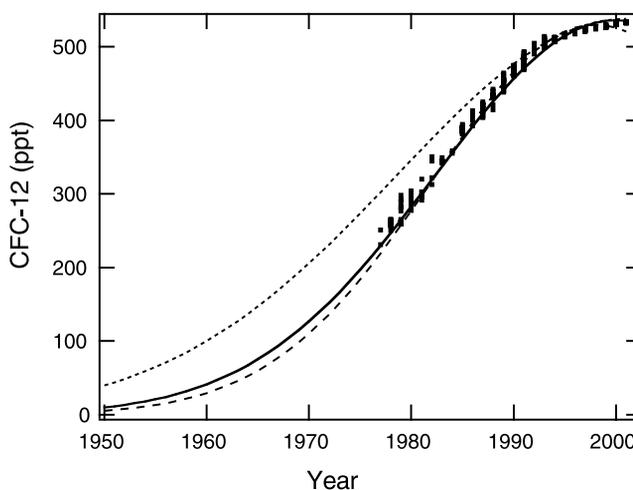
[25] A close examination of the middle and deeper part of the concentration profile (from 30 to 100 m) reveals some fluctuation superimposed on any long-term trend in the concentration with depth. This fluctuation seems similar for methyl chloride, ethane and propane. Ethane and propane are measured both on a FID detector with gas chromatography, while methyl chloride and CFC-12 were measured by an ECD detector. Therefore this coherent variation seems not to be caused by the sampling or detection.

[26] In order to test whether the fluctuation in the concentration profiles was the result of regular long-term variability in the records we tried to fit the data to sine functions with periods ranging from 1 to 10 years superimposed on the time series for these gases in the diffusion model. However this could not completely explain the observed variability in the concentration profiles. Instead, it appears that fluctuations at the surface diffuse strongly to yield a smooth gradual concentration gradient in the lower parts of the column. Although we could not find a simple explanation for the observed co-variances in the concentration profiles, they are within the  $1\sigma$  range of the measurements, so we choose to ignore them in order to obtain time series for the gases of Figure 6. For this purpose we used the inverse modelling method described in section 3.2 using a linear time series for the NMHCs and methyl chloride to retrieve the concentration profiles shown in Figure 6. Superimposed on these linear time series we placed a sine function to account only for the seasonal variations of the NMHCs and methyl chloride.

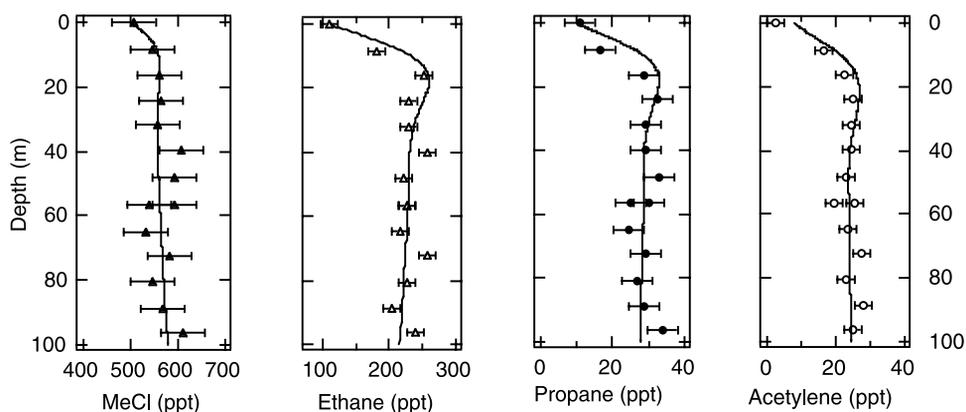
[27] Our computed profiles generally agree well with the observations (Figure 6). These profiles yielded the time series for ethane, propane, acetylene and methyl chloride in the atmosphere shown in Figure 7. Along with our derived concentrations from Figure 7, Table 3 presents direct atmospheric measurements at South Pole [Clarkson *et al.*, 1997; Khalil and Rasmussen, 1999] and Neumeyer station [Rudolph *et al.*, 1992] at Antarctica and from Cape Grim [Lewis *et al.*, 2001] and Baring Head [Clarkson *et al.*, 1997]. The measurements done by Gros *et al.* [1998] represent marine boundary layer air measured during a cruise in the summer of 1993 and Blake *et al.* [1999] measured marine boundary layer air during an aircraft campaign in 1995. The measured values from these studies

vary strongly with location obscuring a direct comparison. It is therefore important to gain more and longer records for these gases in the Southern Hemisphere. From our firn air analyses we were able to lengthen the records significantly to 25 years for the NMHCs and methyl chloride. The results we added to this list represent free atmospheric concentrations and agree well with the other studies. Although the background concentration for ethane seems to be significantly lower than earlier observations by Rudolph *et al.* [1992] from Neumeyer station over the period 1984–1990. On the other hand, our result, for ethane are in line with the observations from two stations (South Pole and Baring Head) measured by Clarkson *et al.* [1997] and the marine boundary layer air measured by Gros *et al.* [1998].

[28] Because this is the first time that NMHC are analysed from firn air, some indication about the stability of these gases in the firn layer is needed. Seinfeld and Pandis [1998] describe the tropospheric chemistry of NMHC to be highly reactive to OH radicals and other oxidizing species. Dibb *et al.* [2002], Swanson *et al.* [2002], Sumner *et al.* [2002] and Honrath *et al.* [2002] describe the concentration of reactive gases in the snow layer and emission of OH radicals and other reactive gases like NO<sub>x</sub>, HONO, HNO<sub>3</sub> from the snow pack into the atmosphere above an ice cap. Reactions of NMHC and methyl chloride with these emitted oxidizing species like OH might therefore explain the low concentration in the atmosphere of the NMHC over Antarctica. Though deeper in the firn layer, reactions with these oxidizing species are not to be expected because of the following: (1) OH radicals are photochemically produced



**Figure 5.** Representation of the CFC-12 atmospheric history over Dronning Maud Land derived from firn air including the upper and lower limit due to the uncertainties in the measured profile ( $1\sigma$ ) and diffusion scaling factor (Table 1). The short-dashed line represents the upper limit, and the lower limit is presented as a long-dashed line. Both limits give a concentration profile deviating  $+1\sigma$  and  $-1\sigma$ , respectively, from the measured profile. The solid line represents the time series that yielded the best fit through the measured concentration profile (Figure 4). The model results are plotted together with NOAA South Pole measurements [Prinn *et al.*, 2000].



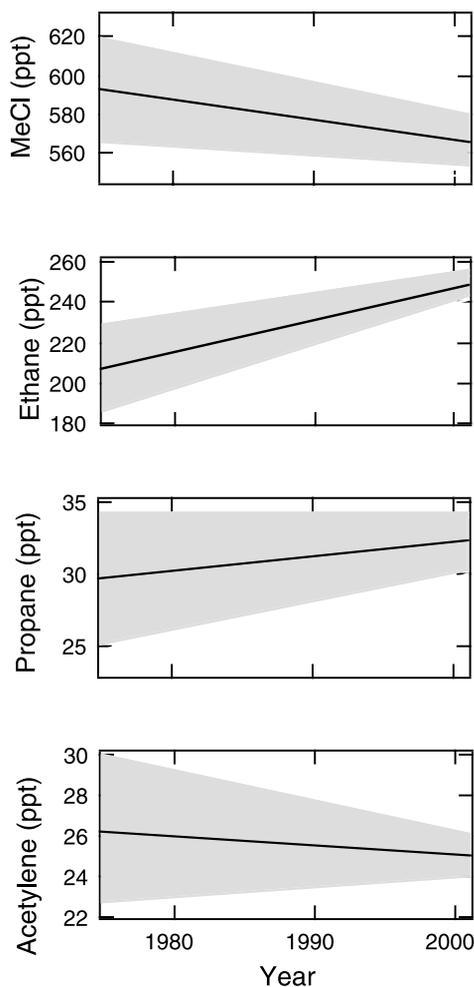
**Figure 6.** Concentration profiles for methyl chloride, ethane, propane and acetylene. The solid line shows the optimal result from the diffusion model forced with a linear time trend at the surface (shown in Figure 7 as solid lines) with seasonal variations as forced upon the linear time series.

and sunlight only penetrates the snow layer for less than 1 m [Warren, 1982]. We can therefore safely assume that there will be no formation of OH radicals deeper in the firn layer. (2) The lifetime of OH radicals in the atmosphere is only a few seconds [Seinfeld and Pandis, 1998]; therefore it is safe to assume that the OH radicals will not diffuse deep in the firn layer and that reactions with these radicals are insignificant at 8 m depth (first firn air measurement). This concept is confirmed by Swanson *et al.* [2002], who showed the concentration profile of ethane and propane from 0–2 m in the snow and firn on Summit (Greenland). Their profiles do not show any loss or production in this part of the firn.

[29] Below this upper zone, NMHC, are stored in the firn layer, which is a dark and cold environment. We can therefore expect that these gases remain stable in concentration simply because of the lack of reactive oxidizing gases and radicals like OH. We assume that the firn air concentrations represents smoothed mean annual concentrations except for the first 20 m from the surface, which is influenced by the seasonal variations.

[30] Linear trends of ethane, propane, acetylene and methyl chloride over the past 25 years (1975–2000) over DML are presented in Figure 8. For methyl chloride we derived a decrease of  $1.2 \pm 0.6$  ppt per year. A study of methyl chloride by Khalil and Rasmussen [1999] reports a similar decreasing trend; the concentrations measured at South Pole between 1984 and 1994 according to Table 3 varied between 477 and 596 ppt. The trends observed for several locations in that study however strongly deviate from the average global trend. Butler *et al.* [1999] performed a firn air study at South Pole. In their study they found an increasing trend from the beginning of the twentieth century to the 1970s. From approximately 1975 to 1999, their derived history for methyl chloride seems to stabilize and becomes more comparable to our data, though Butler *et al.* [1999] had derived a somewhat lower concentration range of 480–521 ppt for the same period (1975–1999) (Table 3). Because of the uncertainties for measuring methyl chloride our obtained concentration range is inline with the other studies for this gas.

[31] A nearly constant level for acetylene and propane was derived for the period of 1975–2000. These gases are produced mainly by biomass burning and fossil fuel use.



**Figure 7.** Extracted time series for methyl chloride (MeCl), ethane, propane and acetylene from the modeled concentration profiles. The gray areas present solutions yielding concentration profiles within  $1\sigma$  of the measured concentration profile. Uncertainties for the diffusion scaling parameter (Table 1) are taken into account. These time series represent the yearly mean surface concentration over DML between 1975 and 2001. The linear trends of these time series are given in Figure 8.

**Table 3.** Annual Mean Concentrations for Ethane (C<sub>2</sub>H<sub>6</sub>), Propane (C<sub>3</sub>H<sub>8</sub>), Acetylene (C<sub>2</sub>H<sub>2</sub>), and Methyl Chloride (CH<sub>3</sub>Cl) Measured at Different Remote Locations in the Southern Hemisphere for Comparison With the Obtained Annual Surface Concentrations for the Period of 1975–2000 Over DML (Site M)<sup>a</sup>

| Period         | Annual Concentrations, ppt    |                               |                               |                      | Location                           | Reference                          |
|----------------|-------------------------------|-------------------------------|-------------------------------|----------------------|------------------------------------|------------------------------------|
|                | C <sub>2</sub> H <sub>6</sub> | C <sub>3</sub> H <sub>8</sub> | C <sub>2</sub> H <sub>2</sub> | CH <sub>3</sub> Cl   |                                    |                                    |
| Jan.–Feb. 1999 | 142 <sup>b</sup>              | 8.8 <sup>b</sup>              |                               |                      | Cape Grim, Tasmania                | <i>Lewis et al.</i> [2001]         |
| 1991–1996      | 296                           | 38                            |                               |                      | Baring Head, New Zealand           | <i>Clarkson et al.</i> [1997]      |
| 1990–1996      | 288                           | 43                            |                               |                      | Scott base, Antarctica             | <i>Clarkson et al.</i> [1997]      |
| Cruise 1993    | 291 ± 76 <sup>b</sup>         | 61 ± 53 <sup>b</sup>          | 48 ± 35 <sup>b</sup>          |                      | SH Ocean 43°–77°S                  | <i>Gros et al.</i> [1998]          |
| Aircraft 1995  | 300–360 <sup>c</sup>          | 6–12 <sup>c</sup>             | 15–30 <sup>c</sup>            | 540–560 <sup>c</sup> | SH Ocean 40°–60°S                  | <i>Blake et al.</i> [1999]         |
| 1982–1990      | 380–400                       | 50–84                         |                               |                      | Neumeyer, Antarctica               | <i>Rudolph et al.</i> [1992]       |
| 1984–1990      |                               |                               | 10–20                         |                      | Neumeyer, Antarctica               | <i>Rudolph et al.</i> [1992]       |
| 1984–1994      |                               |                               |                               | 477–596              | South Pole, Antarctica             | <i>Khalil and Rasmussen</i> [1999] |
| 1975–1999      |                               |                               |                               | 480–521              | South Pole, Antarctica, Firn Air   | <i>Butler et al.</i> [1999]        |
| 1975–2000      | 172–253                       | 21–34                         | 21–30                         | 532–627              | Site M (75°S, 15°E, 3500 m a.s.l.) | this work                          |

<sup>a</sup>Values for methyl chloride have been corrected according to *Montzka et al.* [2003].

<sup>b</sup>Summer values.

<sup>c</sup>November and December values.

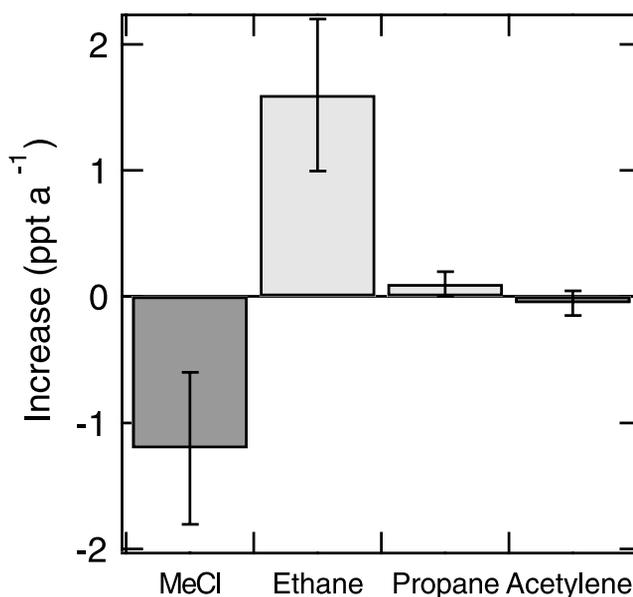
However propane and, to a lesser extent, acetylene [*Kanakidou et al.*, 1988] are also emitted by the ocean [*Lewis et al.*, 2001], which is the only local source for our samples. The measurements for propane and acetylene can therefore only be used to determine background concentrations over DML, as the lifetime for these gases is only 1 month in the atmosphere [*Boissard et al.*, 1996].

[32] In contrast to acetylene and propane, the concentration of ethane appears to have increased in the troposphere ( $1.6 \pm 0.6$  ppt per year). Because of the longer lifetime of ethane ( $\tau = 92$  days in the atmosphere) relative to propane and acetylene, transport from a larger area can be expected [*Boissard et al.*, 1996] and, hence, a stronger influence of biomass burning and natural gas use. According to the IPCC report [*Houghton et al.*, 2001], the use of land has changed significantly in the Southern Hemisphere in the last 25 years, leading to an increase in biomass burning and fossil fuel use. This is consistent with increased NMHC emission from these anthropogenic sources [*Rudolph et al.*, 1992; *Clarkson et al.*, 1997], yielding the increasing trend observed for ethane in the Antarctic firn.

## 5. Conclusions

[33] We used a measured concentration profile for CO<sub>2</sub> and the South Pole atmospheric measurements to optimize a numerical diffusion model, and determined the mean age of CO<sub>2</sub> at pore close-off to be  $28 \pm 3$  years. An inverse modeling approach, verifying the CFC-12 measurements, was used to retrieve time series from the measured concentration profiles in firn for ethane, propane and acetylene, yielding the atmospheric trends for these gases between 1975 and 2000 over DML. Background concentrations of  $24 \pm 2$  ppt for acetylene and  $30 \pm 4$  ppt for propane appeared fairly constant during the past 25 years. In contrast to acetylene and propane, methyl chloride and ethane show significant trends. We derived an increase of ethane, of  $1.6 \pm 0.6$  ppt per year with a background surface concentration of  $241 \pm 12$  ppt in 2000. This background concentration seems to be significantly lower than earlier observations by *Rudolph et al.* [1992] for Neumayer station over the period 1984–1990. On the other hand, the ethane result is consistent with the observations by *Clarkson et al.* [1997] and

*Gros et al.* [1998]. For methyl chloride analyzed from firn air, we deduced a background surface concentration of  $548 \pm 32$  ppt in 2000 and a decrease of  $1.2 \pm 0.6$  ppt per year over the past 25 years. This result is in reasonable agreement with earlier published observations by *Khalil and Rasmussen* [1999] and *Butler et al.* [1999] for the period between 1976 and 1999 given the expected variability in this gas. The concentration range for methyl chloride from Butler et al.'s study appears to be a slightly lower (480–521 ppt; from 1900 to 1999) than our results. Clearly, more extracted time series from firn air analyses in combination with atmospheric chemical transport models are needed to study the atmospheric trends of methyl chloride and light NMHCs over the Southern Hemisphere during the last decades.



**Figure 8.** Results from the model calculations, representing the linear trend in atmospheric surface concentration over Dronning Maud Land in the past 25 years (1975–2000). The error bars represent the modeled upper and lower limits as shown in Figure 7.

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## References

- Blake, N. J., et al. (1999), Aircraft measurements of the latitudinal, vertical, and seasonal variations of NMHCs, methyl nitrate, methyl halides, and DMS during the First Aerosol Characterization Experiment (ACE 1), *J. Geophys. Res.*, *104*(D17), 21,803–21,817.
- Boissard, C., B. Bonsang, M. Kanakidou, and G. Lambert (1996), TROPOZ II: Global distributions and budgets of methane and light hydrocarbons, *J. Atmos. Chem.*, *25*, 115–148.
- Bräunlich, M., O. Aballain, T. Marik, P. Jöckel, C. A. M. Brenninkmeijer, J. Chappellaz, J.-M. Barnola, R. Mulvaney, and W. T. Sturges (2001), Changes in the global atmospheric methane budget over the last decade inferred from <sup>13</sup>C and D isotopic analysis of Antarctic firn air, *J. Geophys. Res.*, *106*(D17), 20,465–20,481.
- Butler, J. H., M. Battle, M. L. Bender, S. A. Montzka, A. D. Clarke, E. S. Saltzman, C. M. Sucher, J. P. Severinghaus, and J. W. Elkins (1999), A record of atmospheric halocarbons during the twentieth century from polar firn air, *Nature*, *399*, 749–755.
- Clarkson, T. S., R. J. Martin, and J. Rudolph (1997), Ethane and propane in the southern marine troposphere, *Atmos. Environ.*, *31*, 3763–3771.
- Dibb, J. E., M. Arsenault, M. C. Peterson, and R. Honrath (2002), Fast nitrogen oxide photochemistry in Summit, Greenland snow, *Atmos. Environ.*, *36*, 2501–2511.
- Fabre, A., J.-M. Barnola, L. Arnaud, and J. Chappellaz (2000), Determination of gas diffusivity in polar firn: Comparison between experimental measurements and inverse modeling, *Geophys. Res. Lett.*, *27*(4), 557–560.
- Gros, V., D. Martin, N. Poisson, M. Kanakidou, B. Bonsang, F. le Guern, and E. Demont (1998), Ozone and C<sub>2</sub>–C<sub>5</sub> hydrocarbon observations in the marine boundary layer between 45°S and 77°S, *Tellus, Ser. B*, *50*, 430–448.
- Honrath, R. E., Y. Lu, M. C. Peterson, J. E. Dibb, M. A. Arsenault, N. J. Cullen, and K. Steffen (2002), Vertical fluxes of NO<sub>x</sub>, HONO and HNO<sub>3</sub> above the snowpack at Summit, Greenland, *Atmos. Environ.*, *36*, 2629–2640.
- Houghton, J. T., Y. Ding, D. J. Griggs, M. Noguer, P. J. van der Linden, X. Dai, K. Maskell, and C. A. Johnson (2001), *Climate Change 2001: The Scientific Basis*, chap. 3, Cambridge Univ. Press, New York.
- Kanakidou, M., B. Bonsang, J. C. Le Rouley, G. Lambert, D. Martin, and G. Sennequier (1988), Marine source of atmospheric acetylene, *Nature*, *335*, 51–52.
- Keene, W. C. (1999), Composite global emissions of reactive chlorine from anthropogenic and natural sources: Reactive chlorine emission inventory, *J. Geophys. Res.*, *104*(D7), 8429–8440.
- Khalil, M. A. K., and R. A. Rasmussen (1999), Atmospheric methyl chloride, *Atmos. Environ.*, *33*, 1305–1321.
- Lewis, A. C., L. J. Carpenter, and M. J. Pilling (2001), Nonmethane hydrocarbons in Southern Ocean boundary layer air, *J. Geophys. Res.*, *106*(D5), 4987–4994.
- Mak, J. E., and C. A. M. Brenninkmeijer (1994), Compressed air sample technology for isotopic analysis of atmospheric carbon monoxide, *J. Atmos. Oceanic Technol.*, *11*, 425–431.
- Montzka, S. A., J. M. Butler, R. C. Myers, T. M. Thompson, T. H. Swanson, A. D. Clarke, L. T. Lock, and J. W. Elkins (1996), Decline in tropospheric abundance of halogen from halocarbons: Implication for stratospheric ozone depletion, *Science*, *272*, 1318–1322.
- Montzka, S. A., et al. (2003), Controlled substances and other source gases, in *Scientific Assessment of Ozone Depletion: 2002, Global Ozone Res. Monit. Proj.* *47*, chap. 1, p. 1.13, World Meteorol. Organ., Geneva.
- Perry, R. H., and C. H. Chilton (Eds.) (1973), *Chemical Engineers Handbook*, 5th ed., pp. 230–234, McGraw-Hill, New York.
- Prinn, R. G., et al. (2000), A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE, *J. Geophys. Res.*, *105*(D14), 17,751–17,792.
- Ramonet, M., et al. (2002), Three years of aircraft-based trace gas measurements over the Fyodorovskoye southern taiga forest, 300 km north-west of Moscow, *Tellus, Ser. B*, *54*, 713–734.
- Rudolph, J., A. Khedim, T. Clarkson, and D. Wagenbach (1992), Long-term measurements of light alkanes and acetylene in the Antarctic troposphere, *Tellus, Ser. B*, *44*, 252–261.
- Scheeren, H. A., J. Lelieveld, J. A. de Gouw, C. van der Veen, and H. Fischer (2002), Methyl chloride and other chlorocarbons in polluted air during INDOEX, *J. Geophys. Res.*, *107*(D19), 8051, doi:10.1029/2001JD001121.
- Schwander, J. (1989), The transformation of snow to ice and occlusion of gases, in *The Environmental Record in Glaciers and Ice Sheets*, edited by H. Oeschger and C. C. Langway Jr., pp. 53–67, John Wiley, New York.
- Schwander, J., J.-M. Barnola, C. Andrieu, M. Leuenberger, A. Ludin, D. Raynaud, and B. Stauffer (1993), The age of the air in the firn and ice at Summit, Greenland, *J. Geophys. Res.*, *98*(D2), 2831–2838.
- Seinfeld, J. H., and S. N. Pandis (1998), *Atmospheric Chemistry and Physics*, John Wiley, New York.
- Siegenthaler, U., H. Friedli, H. Loetscher, E. Moor, A. Neftel, H. Oeschger, and B. Stauffer (1988), Stable-isotope ratios and concentration of CO<sub>2</sub> in air from polar ice cores, *Ann. Glaciol.*, *10*, 1–6.
- Sillman, S., et al. (1995), Photochemistry of ozone formation in Atlanta, GA: Models and measurements, *Atmos. Environ.*, *29*, 3055–3066.
- Spahni, R., J. Schwander, J. Flückiger, B. Stauffer, J. Chappellaz, and D. Raynaud (2003), The attenuation of fast CH<sub>4</sub> variations recorded in polar ice cores, *Geophys. Res. Lett.*, *30*(11), 1571, doi:10.1029/2003GL017093.
- Sturges, W. T., H. P. McIntyre, S. A. Penkett, J. Chappellaz, J.-M. Barnola, R. Mulvaney, E. Atlas, and V. Stroud (2001), Methyl bromide, other brominated methanes, and methyl iodide in polar firn air, *J. Geophys. Res.*, *106*(D2), 1565–1606.
- Sturrock, G. A., D. M. Etheridge, C. M. Trudinger, and P. J. Fraser (2002), Atmospheric histories of halocarbons from analysis of Antarctic firn air: Major Montreal Protocol species, *J. Geophys. Res.*, *107*(D24), 4765, doi:10.1029/2002JD002548.
- Sumner, A. L., et al. (2002), Atmospheric chemistry of formaldehyde in the Arctic troposphere at polar sunrise, and the influence of the snowpack, *Atmos. Environ.*, *36*, 2553–2562.
- Swanson, A. L., N. J. Blake, J. E. Dibb, M. R. Albert, D. R. Blake, and F. S. Rowland (2002), Photochemically induced production of CH<sub>3</sub>Br, CH<sub>3</sub>I, C<sub>2</sub>H<sub>5</sub>I, ethene, and propene within surface snow at Summit, Greenland, *Atmos. Environ.*, *36*, 2671–2682.
- Van den Broeke, M. R., J.-G. Winther, E. Isaksson, J. F. Pinglot, L. Karlof, T. Eiken, and L. Conrads (1999), Climate variables along a traverse line in Dronning Maud Land, East Antarctica, *J. Glaciol.*, *45*(150), 295–302.
- Warren, S. G. (1982), Optical properties of snow, *Rev. Geophys.*, *20*(1), 67–89.
- Wilke, C. R., and C. Y. Lee (1955), Estimation of diffusion coefficients for gases and vapours, *Ind. Eng. Chem.*, *47*, 1253–1257.
- Winther, J.-G., et al. (2002), European Project for Ice Coring in Antarctica (EPICA): Nordic traverse in 2000/01, in *Norwegian Antarctic Research Expedition 2000/01*, edited by J.-G. Winther, *Norsk Polarinst. Rep. Ser.*, *120*, 18–29.

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